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A weight loss technique for the determination of phase boundaries

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A WEIGHT LOSS TECHNIQUE FOR THE DETERMINATION OF PHASE BOUNDARIES

BY

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THESIS

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ABSTRACT

An apparatus has been designed and constructed that would continuously record the weight loss of a sample in a flowing inert atmosphere, at a constant temperature.

A technique has been developed to determine the phase boundaries of a binary phase diagram.

Alloys of the magnesium-nickel, cadmium-antimony, copper-cadmium, copper-zinc, and magnesium-zirconium systems were subjected to investigation to verify the operation and resolve a number of limitations of the equipment.

These investigations disclosed that the apparatus gave the best results with alloys having vapor pressures in the range between 1 and 35 millimeters of mercury.

ACKNOWLEDGMENTS

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I. INTRODUCTION

Phase diagrams have become an important part of metallurgy and the methods of determining the phase boundaries are numerous.

Difficulties are often encountered, using present techniques, in determining the phase boundaries of binary diagrams containing moderately volatile elements, because of the weight losses incurred during the experiments.

Problems are further compounded if the metal vapor reacts with oxygen to form metal oxides. These difficulties often lead to disagreement between the results of various investigators regarding the location of a phase boundary.

The Federal Bureau of Mines became interested in developing a method for determining phase boundaries that would eliminate the difficulties resulting from the weight loss of the volatile constituent. A convenient method of accomplishing this would be to employ the weight loss to determine the phase boundaries. This would entail the construction of an apparatus that would continuously record the weight loss of a specimen, in an inert atmosphere, at a constant temperature. The weight loss record could then be examined for deviations in the record that would indicate the intersection of a phase boundary.

The object of this investigation was to design and construct equipment that would continuously record the weight loss of a specimen and develop a technique for the determination of a phase boundary of a binary diagram, from the record of the weight loss.

II. REVIEW OF LITERATURE

Because the problem involves the utilization of vapor pressure in an attempt to establish the liquidus line of a binary diagram, a brief resume of the methods of measuring vapor pressure are presented here.

Since 1803, when Dalton first started measuring vapor pressure and relating it to the other properties of substances, many techniques have been devised to measure the vapor pressures of substances. The experimental methods generally used for vapor pressure study fall into three categories, namely: 1. Static; 2. Effusion; and 3. Dynamic methods.

Since there are numerous methods of vapor pressure study,[1] only a few typical examples of each category will be discussed, together with possible application to the present problem.

Static methods would be the most desirable. Since equilibrium is reached between the vapor and the melt under static conditions and since a constitution diagram is a representation of an equilibrium condition, these methods would more truly represent the system.

Two static methods are chosen as examples, the first of which is the spectrographic technique similar to the method used by Herbenar, Siebert, and Duffendack[2] for the measurement of zinc vapor pressure of alpha brasses. In this method the sample being studied is placed in a sealed absorption cell of transparent silica, brought up to temperature, and light emitted from an arc is passed through the portion of the cell containing the zinc vapor. Since the intensity of certain radiation transmitted is a measure of the amount of vapor, a relationship between the intensity transmitted and the vapor pressure can be determined.

This technique is good in that it is static; it provides reproducible results; and equilibrium is reached. However, an extremely large number of samples must be run on expensive equipment and the container cannot react with the vapor because the radiation transmission must not be impaired and equilibrium must not be disturbed. This last restriction would exclude the use of this technique for the alkali and alkaline-earth elements such as sodium or magnesium.

The second static method is the dew point method. This method was first used for metals by Hargreaves[3] and is based on the principle that at a certain temperature and pressure a vapor will start to condense.

A sample is placed inside a tube; the tube is evacuated and then sealed. A thermocouple is placed at the sample end and one at the other end of the tube. A thermal gradient is impressed over the length of the tube with the hottest portion being the sample end. The temperature at which the first droplets of condensed vapor appear at the cooler end of the tube as well as the temperature of the sample are recorded. Knowing the temperature-pressure relationship of the vapor involved, one can determine the vapor pressure of the sample.

Some of the better features of this system are that the results are reproducible; the system attains equilibrium; and this method would take fewer samples to determine the liquidus than the spectrographic technique. On the other hand, there are more manipulations involved than in the spectrographic technique and just as in the spectrographic method visibility through the container must be maintained at all times.

The effusion methods seem to be quite reliable in that the results are reproducible and check very closely with some of the other methods used for measuring vapor pressure.

Only the Knudsen[4] method will be discussed here since this method employs most of the principles involved in all the effusion techniques and possesses most of the advantages as well as the disadvantages of effusion methods in general.

This method requires that the substance be enclosed in a container provided with a small orifice of exactly known area. The container with the substance enclosed is weighed before and after heating at the required temperature for a known length of time in a high vacuum. Knowing the weight loss, the amount of time to lose the weight, the molecular weight of the vapor, and the area of the orifice, one can calculate the vapor pressure of the substance in the container.

Most of the effusion methods give fairly reproducible results and are relatively straightforward but are designed for the study of very low vapor pressures; therefore, they are not suitable for this investigation.

Two dynamic methods will be discussed. One of these is the boiling point method first applied to metals by Greenwood[5] and later refined by Ruff[6][7] and Fischer.[8][9] The boiling point method is relatively simple in principle and operation but requires many samples and there are inherent errors in the system which cannot be overcome. The method itself consists of determining the pressure at which the substance will boil at a constant temperature.

The second dynamic method is the transport or carrier gas method which was modified for application to this problem. This method is very commonly applied to organic and inorganic compounds at relatively low temperatures and was first applied to metals at higher temperatures by Wartenberg,[10] then later to alloys by Jellinek.[11]

The principle upon which it is based is relatively simple: An inert gas, preferably of high atomic weight (argon), is passed through a tube furnace over the metal sample and carries away the metal vapor to condense in a cold trap or a cooler part of the system. The vapor pressure of the metal is calculated, using Boyle's law, from the volume of the gas passing through the furnace tube.

The transport method is especially useful for alloys with vapor pressures between 0.1 mm and 100 mm mercury and therefore it is used frequently for magnesium vapor pressure determinations. Schneider and Stoll[12] were the first to apply this method to magnesium alloys with their work on the magnesium-aluminum system. Later Vetter and Kubaschewski[13] applied the method to their work on the magnesium-bismuth and magnesium-antimony system. More recently Schmahl and Sieben[14] used it on the magnesium-copper, magnesium-lead, and the magnesium-nickel systems. Schmahl and Sieben[14] used a thermobalance designed by Schneider together with the firm of Sartorius which enabled them to weigh a specimen in a flowing gas, at atmospheric pressure, inside a horizontal furnace during the heating and cooling periods. This procedure avoided the necessity of estimating the weight losses during these periods and thereby provided more accurate results.

Most of the foregoing methods are used in determining the vapor pressures or activities of the various alloys studied and until recently no attempt was made to continuously volatilize an alloy as a means of finding alloy phase relationships.

Veleckis, Rosen, and Feder[15] using a recording effusion balance, investigated the solid phases of the uranium-cadmium, uranium-zinc, and the cerium-zinc systems.

Their apparatus consisted of a Knudsen effusion cell suspended within an evacuated chamber from one arm of a recording analytical balance. This enabled them to record the sample weight continuously as the volatile constituent escaped from the cell and condensed in a cooler portion of the system. With the weight record, and Langmuir's relationship for the dependency of rate of evaporation on vapor pressure, they were able to derive a continuous record of vapor pressure which they plotted as a function of atomic ratio. An example is shown in Figure 1 for the uranium-zinc system.

The dotted lines superimposed on the figure show the expected equilibrium vapor pressure relationships whereas the solid lines are the observed kinetic ones. The various departures from equilibrium are explained as follows:

(a) The evaporating area is insufficiently large relative to the orifice area.

(b) Evaporation from the surface of a solid solution takes place more rapidly than diffusion within the solid; thus the pressure observed will be characteristic of the composition of the depleted surface.

(c) Evaporation from a homogeneous phase decreases regularly.

(d) Evaporation from a homogeneous phase takes place more rapidly than does nucleation of the succeeding phase, causing supersaturation.

(e) Evaporation from a heterogeneous mixture leads to constant vapor pressure despite changing atomic ratio.

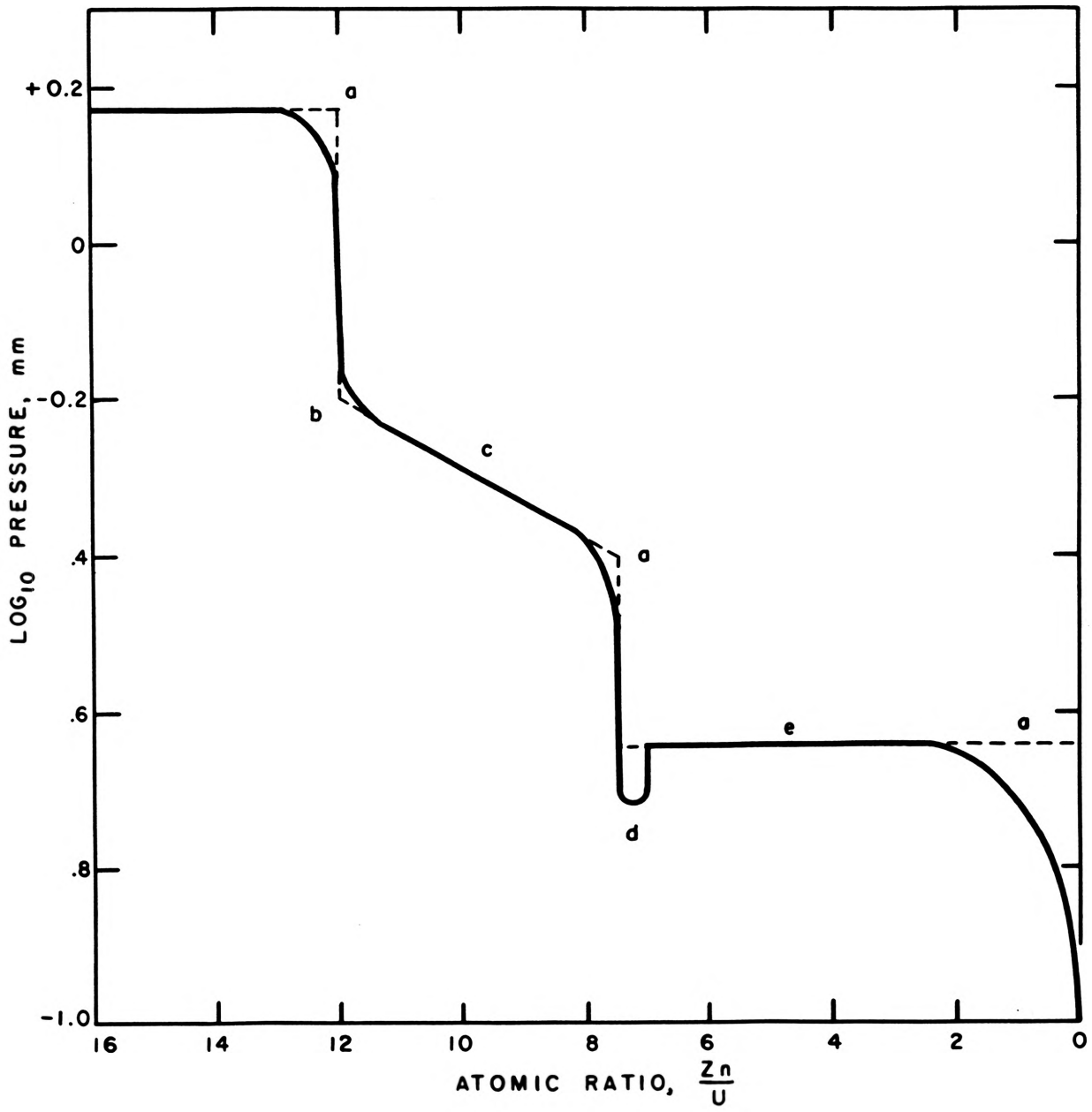

FIGURE 1. – Isothermal Diagram of Logarithm$_{10}$ Vapor Pressure Versus Atomic Ratio.

In spite of the difficulties encountered with solid state diffusion, solid-solid transformation, and unfavorable kinetics of certain solid-vapor reactions, Veleckis, Rosen, and Feder have been able to obtain results that coincide very well with results obtained by other methods.

III. EXPERIMENTAL PROCEDURE

A. Preparation of Alloys

1. Selection of alloying elements

The alloying elements were selected so that there was a minimum of three orders of magnitude difference between the vapor pressures of the two constituents and generally the difference was nine orders of magnitude. A list of the alloying elements together with their approximate vapor pressures, at the temperatures of the experiment, is given in Table I.

2. Purity of alloying elements

Table II lists the analysis of the elements used in making up the various alloys used in this investigation. It will be noted that all the elements, with the exception of zirconium, have purity levels greater than 99.9 percent.

3. Chemical analysis of specimens

As the specimens had to be preshaped to the size of the crucible, filings were taken of the sample itself and then submitted to the analytical laboratories of the Bureau of Mines for chemical analysis.

B. Weight Loss Technique

1. General principles

With the aid of three relationships one can determine the number of phases present within a binary alloy specimen. The first of these is devised from the kinetic theory of gases and relates the rate of weight loss of a specimen to its vapor pressure.

TABLE I

List of alloying elements with their respective vapor pressures

Volatile elements		
Zinc	250 mm Hg	(800° C)
Cadmium	195 mm Hg	(650° C)
Magnesium	5 mm Hg to 32 mm Hg	(700° C - 800° C)
Nonvolatile elements		
Antimony	10^{-2} mm Hg	(840° C)
Copper	$<10^{-8}$ mm Hg	(800° C)
Nickel	$<10^{-8}$ mm Hg	(800° C)
Zirconium	$<10^{-8}$ mm Hg	(800° C)

TABLE II

Analysis of elements used in alloying

Inco 270 Nickel		Single Sublimed Magnesium		Cadmium	
C	0.002	Si	0.01	Zn	0.016
Mn	<0.001	Pb	0.001	Cu	0.0014
Fe	0.002	Ag	0.01	Sn	0.0006
S	0.0008	Cu	0.0005	In	0.001
Si	0.002	Fe	0.003	Ni	0.0055
Cu	<0.001	Zn	0.0004	Au	0.00069
Cr	0.002	Mg	99.975	As	0.00003
Co	0.002			Sb	0.00006
Ni	<99.98			Cd	99.963

High Purity Copper	Antimony		Zirconium	Zinc
Se + S < 0.00001	As	0.03	Added as a master alloy of approximately 35 percent zirconium	Pb + Fe + Cd < 0.01
Cu 99.999	Cu	0.001		Zn 99.99
	Fe	0.01		
	Sn	0.005		
	Pb	0.04		
	Sb	99.91		

This relationship, known as Langmuir's equation* is:

$$G = k\sqrt{\frac{M}{T}}P$$

where G = the rate of evaporation per unit area

k = a constant depending upon the units of P, M, G, T, and the area

M = the atomic mass of the substance volatilizing

T = the absolute temperature

P = the vapor pressure of the specimen.

If an alloy is used in which only one component has an appreciable vapor pressure, the atomic mass (M) becomes a constant. If the area and temperature of the specimen are constant, then G is dependent upon only the vapor pressure.

The second relationship, from thermodynamics, states that the partial pressure of a substance is proportional to the products of the mole fraction and the vapor pressure of the pure component.

$$P_a = \gamma P_o N_a$$

where P_a = the partial pressure of component a

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*NOTE

Langmuir's equation is valid only for experiments conducted in a vacuum where the mean free path of the metal atoms is long in comparison to the experimental apparatus, therefore it would not strictly apply to the present situation, since the transport method incorporates the use of a flowing inert gas at atmospheric pressure.

With the admission of an inert gas at atmospheric pressure the mean free path of the metals atoms is greatly reduced by collisions with the inert gas; thus, a gaseous diffusion coefficient must be considered. This coefficient, a function of the temperature and the pressure of the inert gas, does not alter the linear relationship between the rate of evaporation and the vapor pressure.

Work on gaseous diffusion coefficient for silver and aluminum has been done by Ilschner and Humbert.[16] Therefore, it is assumed that other elements follow the same general relationships as do silver and aluminum.

γ = the proportionality constant, known as the activity coefficient

P_o = the vapor pressure of the pure component a

N_a = the mole fraction of component a.

The final relationship to consider is Gibbs' phase rule which states that the number of degrees of freedom of a system is equal to the number of components in the system minus the number of phases present plus two. The constant, two, accounts for the temperature and total pressure variables.

Symbolically,

$$F = C - P + 2$$

where F = number of degrees of freedom

C = the number of components

P = the number of phases.

If the total pressure is held constant the system loses one degree of freedom and since in binary systems the number of components is two, the phase rule becomes:

$$F = 2 - P + 1$$

If the system has initially a single phase, such as the liquid region, the phase rule shows that the system exhibits two degrees of freedom. Thus, if the temperature is held constant, the composition can still vary without the appearance of an additional phase. If we combine the first and second relationships we see that the rate of weight loss of an alloy specimen will be directly proportional to the mole fraction of the volatile element.

Thus:

$$G = R\gamma P_o \sqrt{\frac{M'}{T}} N_a$$

The phase rule shows that the composition of the system can vary at constant temperature as long as the system is in a single phase. If the metal vapors are continually being carried away, as in the transport method, the composition of the system will vary as there is no chance for equilibrium between the liquid and its vapor. Thus, the rate of weight loss will vary with time as more and more of the system is volatilized. Depicting this graphically as weight of the sample versus time, as in Figure 3, the curve would have a changing slope as shown from (a) to (b).

When the system reaches the liquidus (point b) the phase rule shows the system loses one degree of freedom; therefore, if the temperature is held constant the composition must remain constant along with the rate of weight loss. This means the specimen will continue to lose weight but at a constant rate and the curve of weight versus time will become a straight line with constant slope as shown from (b) to (c).

In a system of which there is only one volatile constituent the composition of the specimen at any point can be calculated from the initial composition and the weight loss up to the point in question. Therefore, this is another method that can be used to determine the composition of the phase boundaries, and thus, we can construct a binary diagram simply by determining the points at which the curves become a straight line. Figure 2 shows the relationship of the binary diagram to the graph of weight versus time.

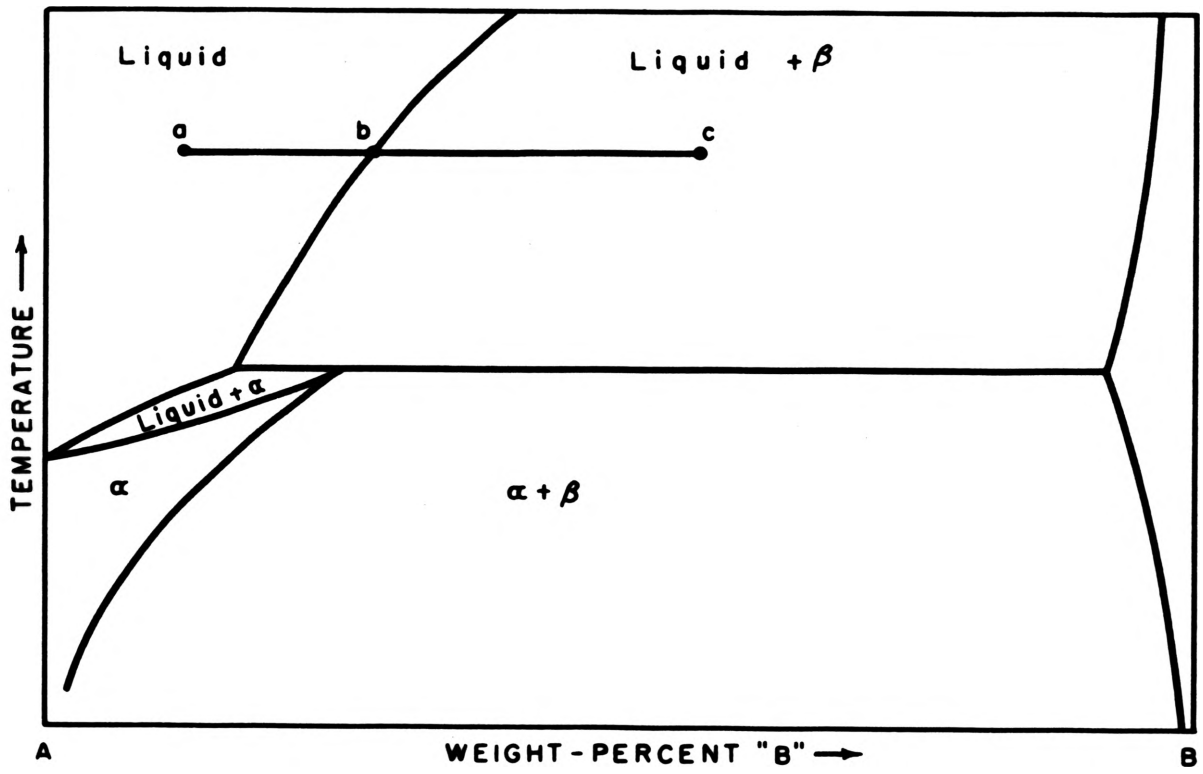

FIGURE 2.-Isobaric Temperature-Composition Diagram.

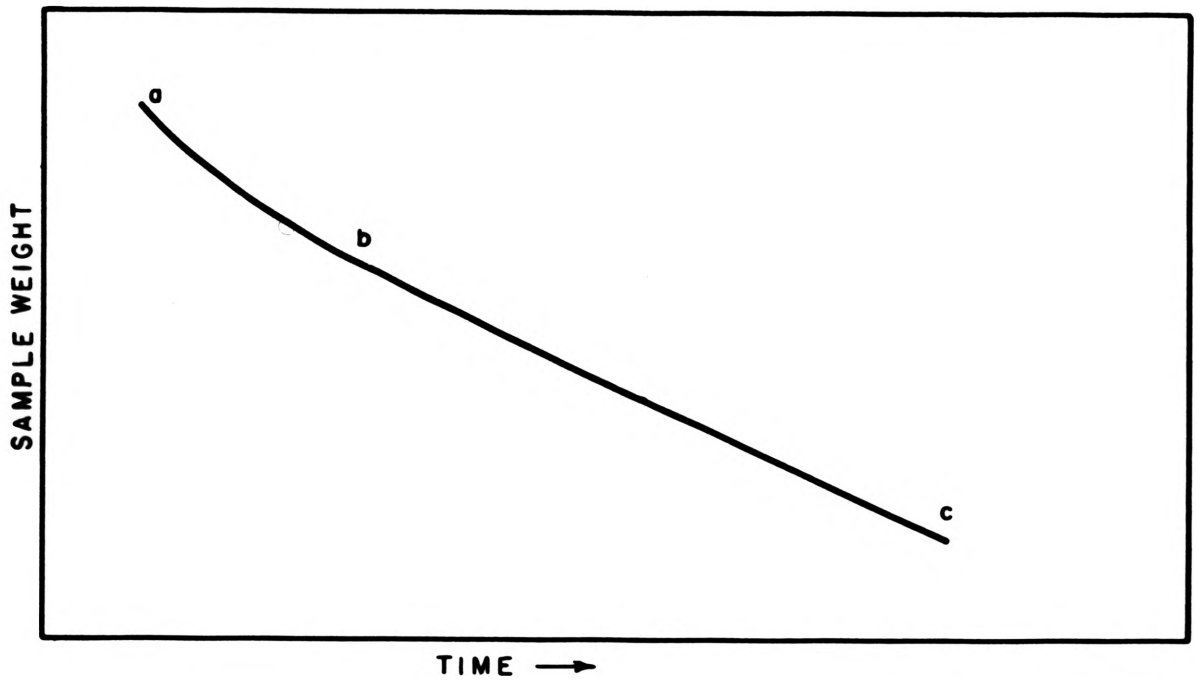

FIGURE 3. - Sample Weight Versus Time.

Figure 4 is a hypothetical isothermal binary diagram of vapor pressure versus composition with points a, b, and c, marked to correspond to those points in Figures 2 and 3.

2. Apparatus

Figure 5 shows schematically a layout of the apparatus used in making measurements of the rate of weight loss of a sample and Figure 6 is a photograph of the same arrangement.

The make, model, and serial number of the standard apparatus are given below:

1. Minneapolis-Honeywell, Brown Electronik Strip Chart Recorder; Model No. K153x11-VH-II-III-27: Serial No. U1182148001;-2 to 20 millivolt full-scale deflection.
2. Voland Analytical Balance; Model No. 220; Serial No. 26975.
3. Fisher Recording Balance Accessory; Model No. 75; Serial No. 146.
4. Marshall Platinum - wound tube furnace; rated for 1300° C, 1-5/8 inch bore, 16 inches long; Serial No. 614322.
5. Leeds and Northrup Micromax temperature controller; Model No. R-30601 - H; Serial No. 475475.

The Marshall furnace was supplied with shunting taps to reduce thermal gradients within the furnace and the use of these reduced the thermal gradients in the specimen chamber to 1.5° C over a six-inch span.

The Micromax controller held the furnace temperature to ± 0.5° C in the temperature range of the experiments. The Fisher Recording Balance Accessory in conjunction with the Minneapolis-Honeywell recorder, the Voland Analytical Balance, and the knife edge assembly could detect sample weight changes of 2 milligrams.

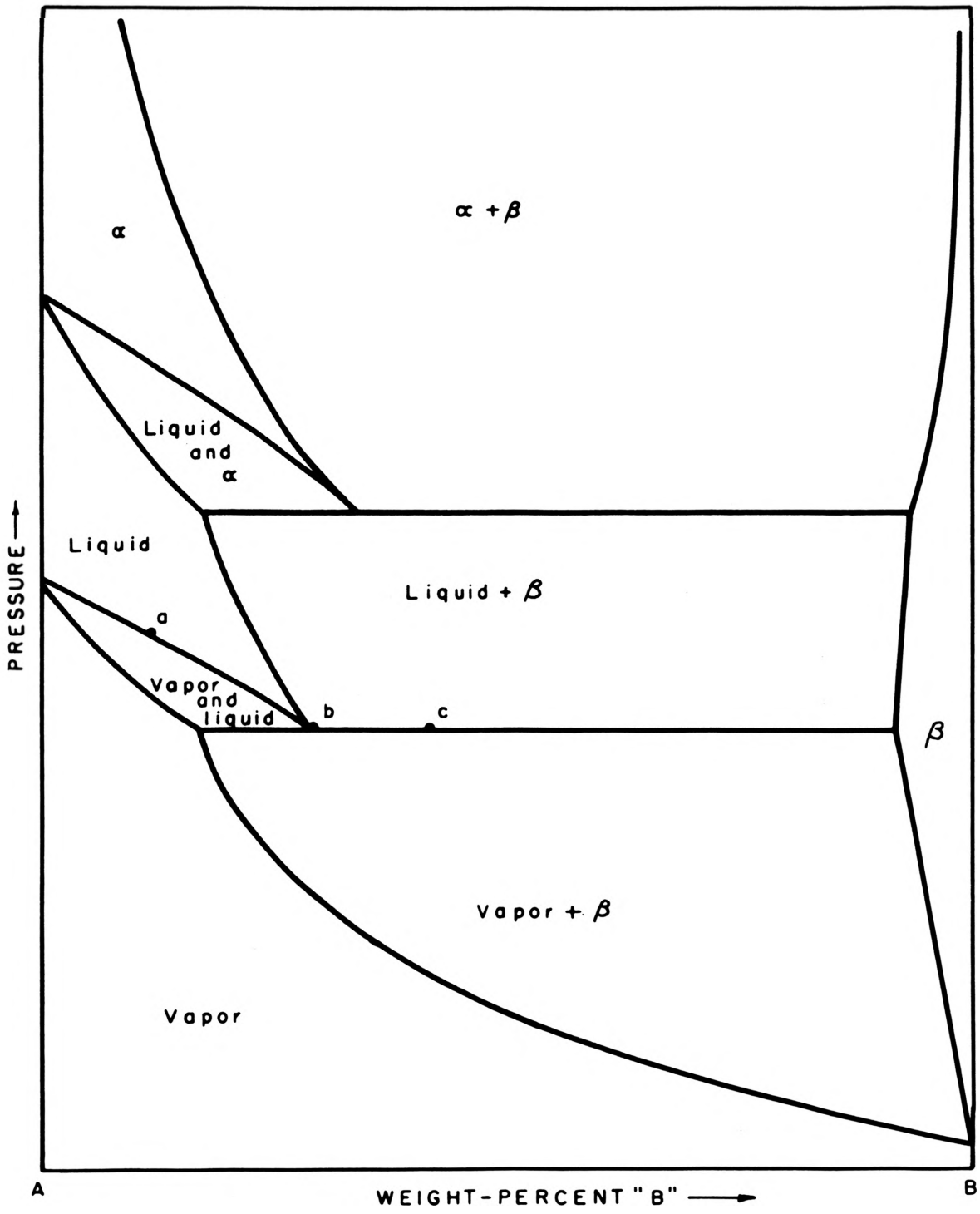

FIGURE 4.-Isothermal Pressure-Composition Diagram.

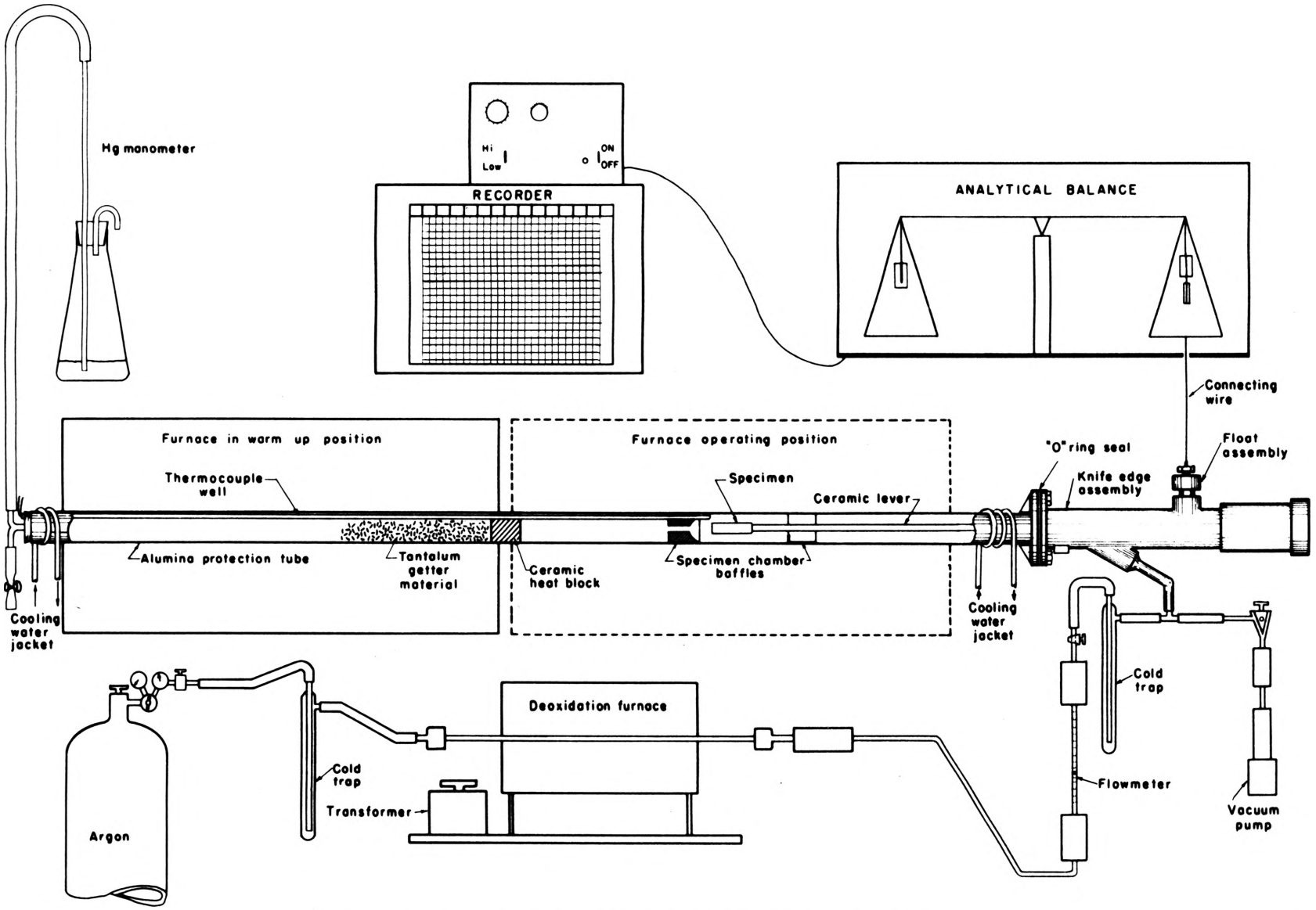

FIGURE 5.- Schematic Diagram of Experimental Apparatus.

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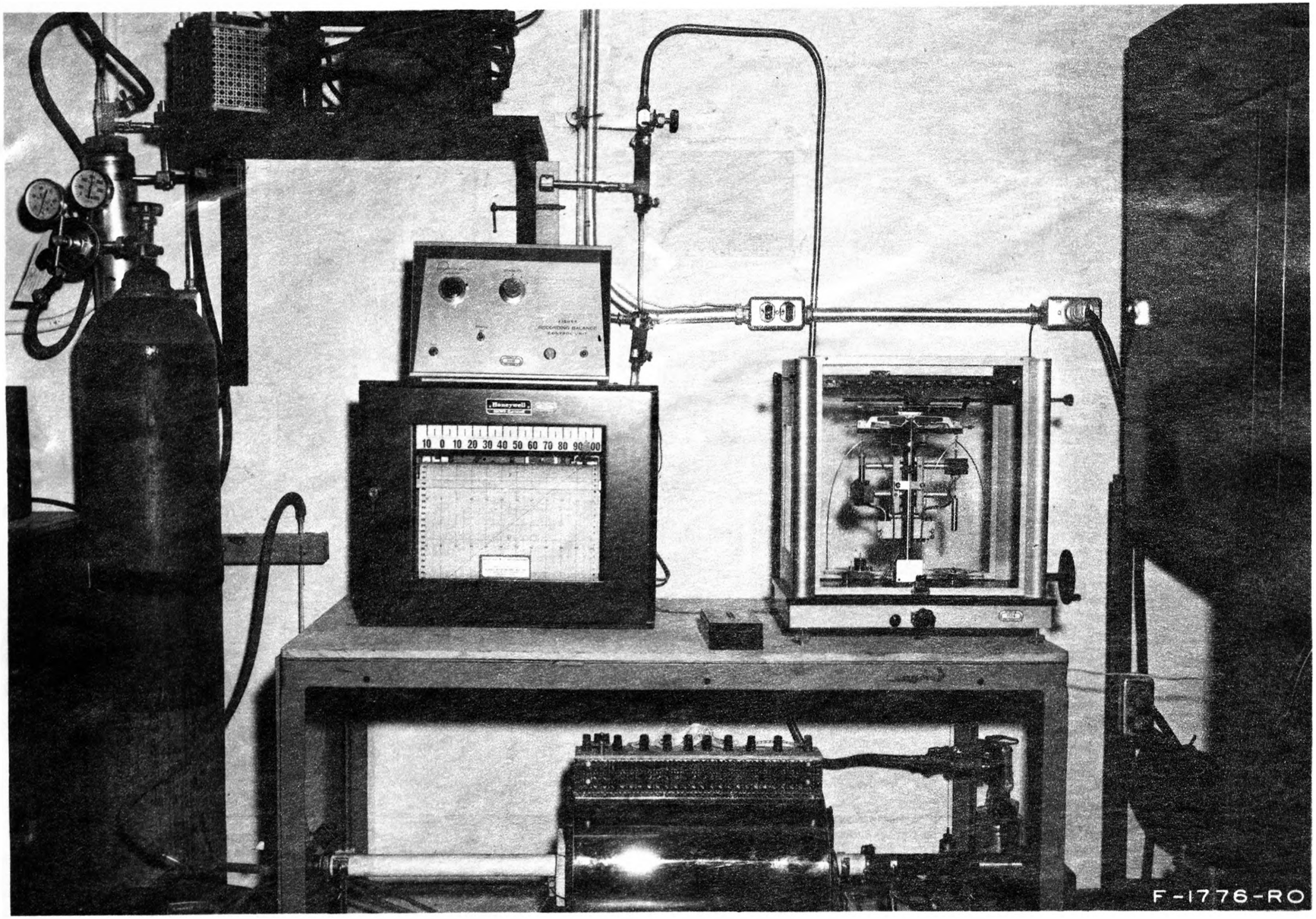

FIGURE 6.—Photograph of Experimental Apparatus.

The knife edge assembly, Figure 7, which had to be designed and fabricated, consists of two major components, the float assembly and the lever arm assembly.

The function of the float assembly is to seal the system during evacuation and flushing, and to act as an air-tight seal that will transmit the weight change of the specimen to the analytical balance during the actual experiment.

In order to minimize oxidation of the specimen the system must be evacuated and flushed a number of times to purge any oxygen and nitrogen within the system. This is accomplished by clamping the assembly as in Figure 8A, then evacuating and back flushing the system at least four times before the argon pressure is brought to atmospheric pressure, the exhaust valve opened and a positive flow of argon is established. The argon is passed over hot calcium chips and through a dry ice-acetone freeze trap for purification. Once a positive flow is established the float assembly is screwed into the operating position by tightening the upper portion of the float assembly against the "O" ring as shown in Figure 8B.

Once in the operating position, the float assembly is able to transmit any weight changes in the specimen to the analytical balance and to continue to maintain a seal by virtue of the oil bath.

The lever arm assembly as shown in Figure 7 consists of two lever arms, one ceramic and one metal, connected by a knife edge. The specimen crucible is supported by the end of the ceramic lever arm and the metal lever arm is connected to the float assembly by way of a connecting bushing. The mechanical advantage of the lever arm assembly is 2.762 to 1.

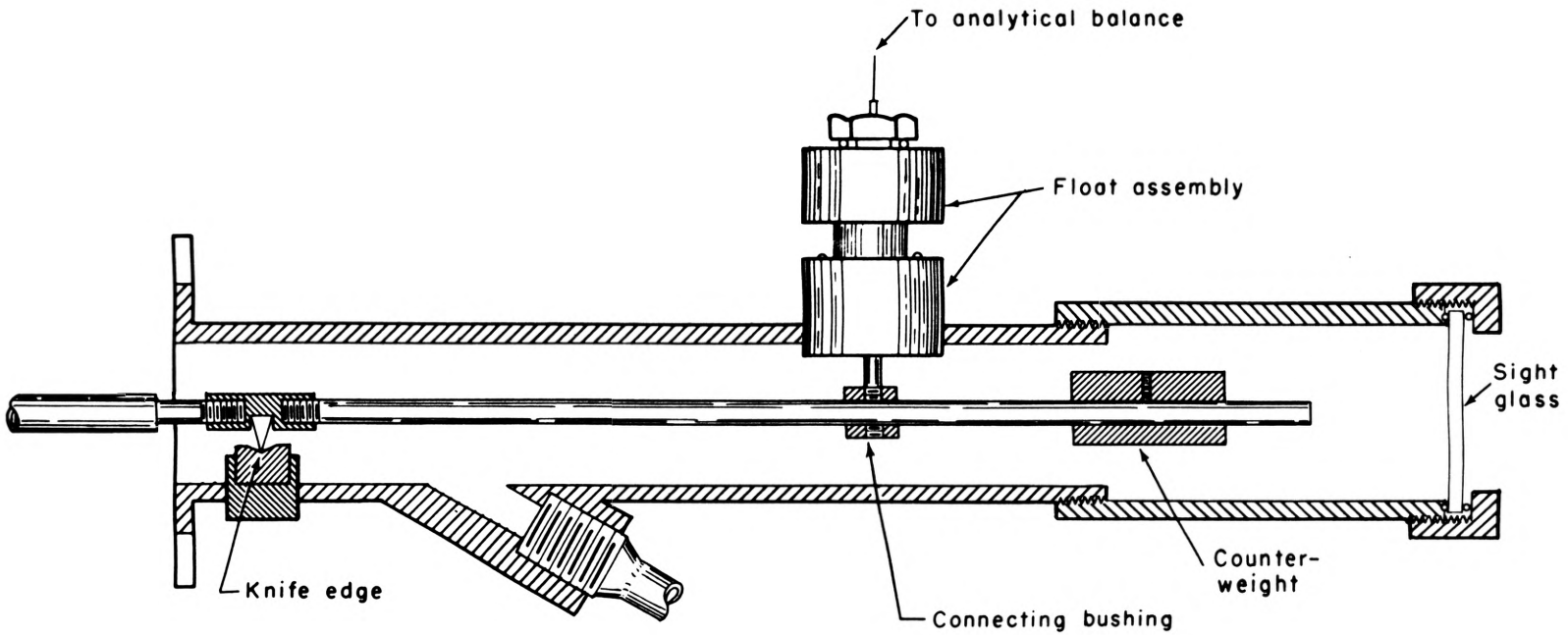

FIGURE 7.- Knife Edge Assembly.

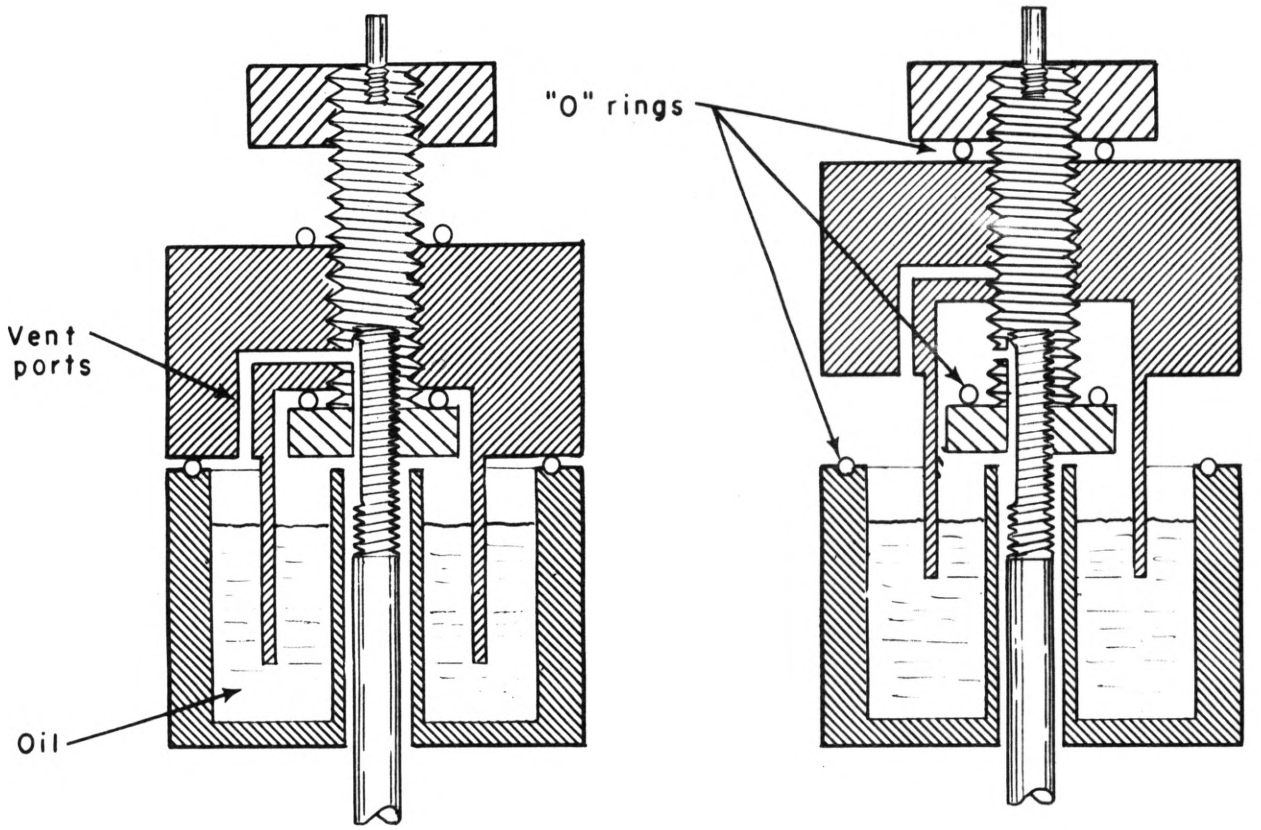

FIGURE 8.- Float Assembly.

Any change in specimen weight is transmitted to the float assembly by the knife edge and in turn is transmitted to the analytical balance.

The analytical balance is equipped with a Fisher Recording Balance accessory, a servomechanism that automatically maintains the equilibrium position of the balance.

The accessory consists essentially of a special linear variable differential transformer assembled in connection with one arm of the balance, an electronic control unit, and a restoring coil and magnet used in connection with the other arm of the balance. Any displacement of the balance pan is detected by the linear variable differential transformer. This transformer produces an AC signal whose phase is dependent on the direction of the deflection. This signal is fed into the electronic control unit which in turn furnishes sufficient current to the restoring coil on the opposite arm of the balance to restore the balance to the equilibrium position. This restoring current is proportional to the weight differential which produced the original deflection. By means of a suitable voltage divider network, the restoring current produces a voltage drop proportional to the weight differential, and this voltage is applied to the recorder to produce a permanent record of the change of weight of the sample. For a complete description and general theory of operation of the Fisher Recording Balance Accessory the reader is referred to a publication of Fisher Scientific Company.(17)

Because the balance is maintained in an equilibrium position at all times, buoyancy effects of the oil on the float assembly can be neglected.

The Minneapolis Honeywell recorder is a linear millivolt recorder with a "floating zero". The millivolt range extends from -2 to 0 to + 20 millivolts, the scale is calibrated from -10 to 0 to + 100 divisions. The balance recording accessory was adjusted so that one gram weight loss of the sample gave a 100 division (10 inch) movement of the recorder. The accessory is connected so that the recording span can be adjusted to any value from 100 milligrams per 100 divisions to 2.5 grams per 100 divisions. In most cases, a sensitivity of 1 gram per 100 divisions was found to be optimum during volatilization. Tare weights were added to the analytical balance pans to bring the recorder back to the starting position. Tare weights were added when the recorder was indicating + 95 divisions thereby returning the recorder pen to -5; thus, dead portions in the record were reduced to a minimum. A 2.762 gram tare weight was needed to offset a one gram weight loss of specimen because of the mechanical advantage of the lever arm assembly.

The specimen crucible is shown in Figure 9. It was fabricated from 0.040 inch thick tantalum with the cross-sectional area held to ± 0.1 percent to limit error in the rate of weight loss due to variation in area. The large exposed surface area of the crucible as well as the shallow depth of the crucible was designed so that the exposed area to volume ratio of the specimen was large enough to minimize concentration gradients arising from slow diffusion processes. Concentration gradients were never observed within specimens with vapor pressures less than 75 millimeters of mercury. Figures 10 and 11 represent the exposed surface and the base, respectively, of a typical example. This specimen lost 49 percent of its original weight yet, with the exception of twinning,

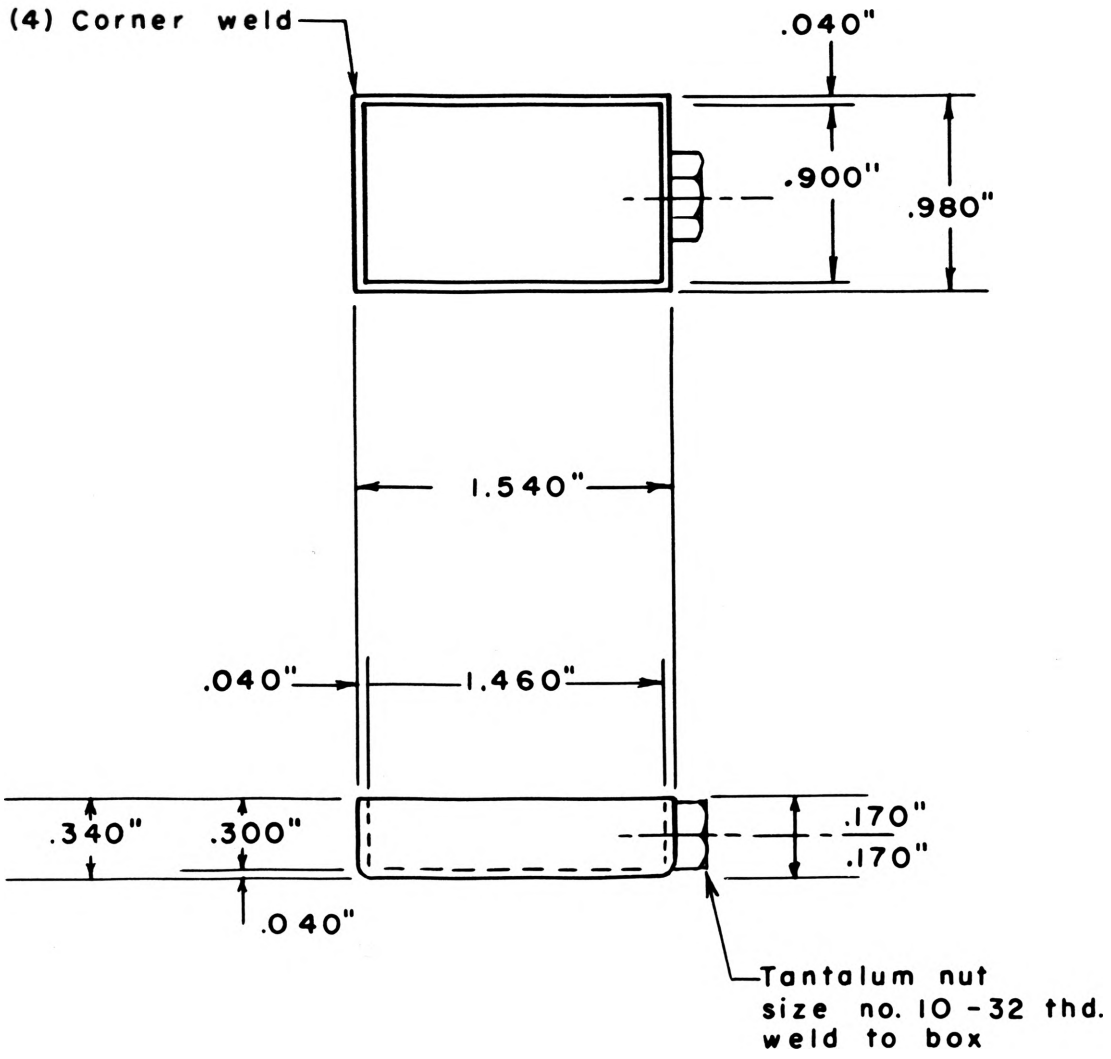

FIGURE 9. – Specimen Crucible.

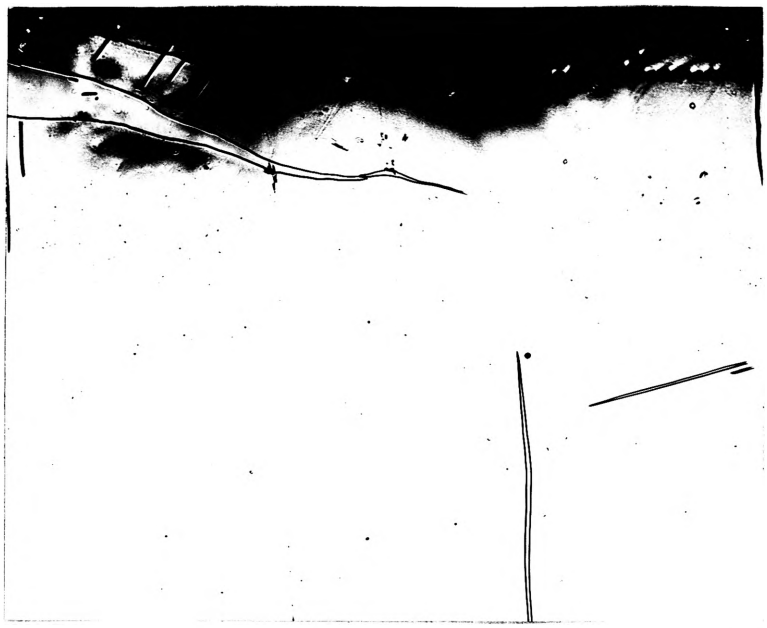

FIGURE 10. Exposed Surface of Mg - 0.37 Percent Zr Specimen, Electrolytically Polished and Etched in Mg 12 for 10 Seconds. X100

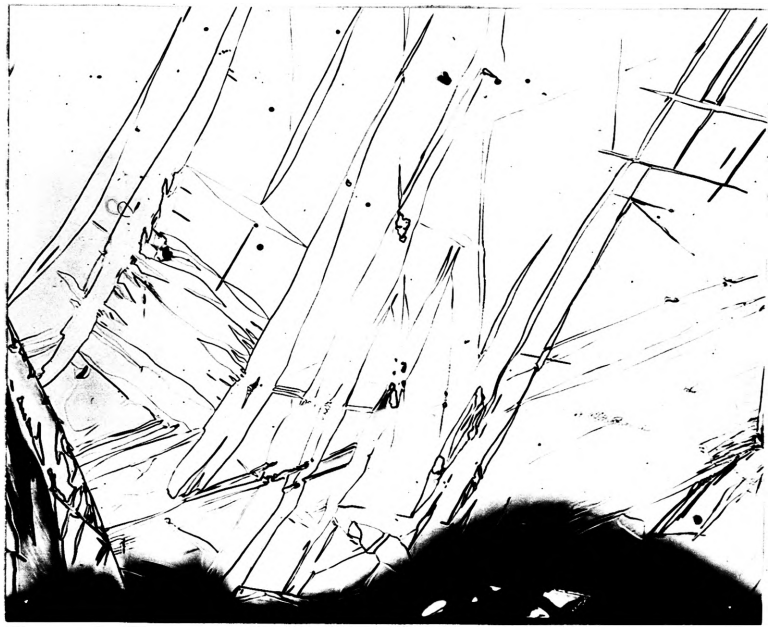

FIGURE 11. Base of Mg - 0.37 Percent Zr Specimen, Electrolytically Polished and Etched in Mg 12 for 10 Seconds. X100

exhibits no noticeable difference in microstructure at the surface, Figure 10, and the base, Figure 11. Although tantalum is relatively inert to most metallic elements some alloying with the sample was noted when a clean crucible was used; therefore, a suitable crucible wash had to be devised to prevent alloying. These crucible washes had varying effects on the specimen and will be discussed more fully later.

3. Preparation of samples

Samples were cut from the center of a cylindrical ingot and shaped to dimensions slightly smaller than the dimensions of the crucible. Samples were then used in the as-cast condition.

4. Procedure

Much of the equipment is in position (see Figure 5) before the sample is placed in the crucible; thus, any oxide formation on the sample at room temperature is minimized.

The back baffle, the tantalum foil getter, and the sample chamber thermocouple are all in place with the furnace in position A and the float assembly is in the evacuation position as previously described, before the sample is placed in the crucible.

The previously shaped sample is cleaned to remove any oxide film and then submerged in acetone to minimize further oxidation. The sample is quickly weighed on an analytical balance and returned to the acetone until it is placed in the crucible. After the sample is placed in the crucible the alumina protection is slid up to within three inches of the knife edge assembly. The front baffle is placed in the protection tube and slid down until it just touches the crucible. The protection tube is slid into the "O" ring seal on the knife edge assembly and secured for evacuation.

The system is evacuated and flushed as previously described; then the float assembly is put into operating position and the system allowed to stabilize for at least four hours before the furnace is preheated in position A.

The furnace in position A is heated as rapidly as possible at a rate of about 550° C per hour, to minimize any preheating of the specimen. When the furnace reaches a temperature 50° C higher than the predetermined experimental temperature it is slid into position B. This procedure enables the specimen to be heated from 70° C, the average starting temperature, to the temperature of the experiment in approximately 15 minutes. During the specimen heating period the argon flow rate is approximately 25 cc/min to minimize specimen losses. Once the sample is at temperature the flow rate is increased to a value between 100 cc/min and 500 cc/min, depending upon the temperature and vapor pressure of the specimen. The maximum flow rate for the apparatus is 500 cc/min. Flow rates greater than this disturb the surface of the specimen causing erroneous results. Higher temperatures usually require lower flow rates to obtain a curve having approximately the 45° slope that is optimum for readability.

Tare weights are added to the balance at proper intervals during the experiment as previously described. The addition of tare weights effectively increases the chart width 10 inches, per traverse, for each tare weight added. Thus, if two tare weights are added, or three grams of specimen lost, during an experiment, the effective chart width is 30 inches or three traverses.

At the completion of a run the furnace is slid back into position A, the flow rate cut to 25 cc/min and air is blown over the specimen area of the protection tube to cool the sample as rapidly as possible and to minimize weight losses during cooling. The cooling rate was approximately the same as the heating rate.

Once the specimen chamber is at room temperature the specimen is quickly removed from the crucible and weighed. This weight is then compared with the recorded weight as a check.

The difference between the recorded weight change and the weight change as measured on an analytical balance is generally of the order of 6 milligrams or approximately 0.02 percent and was never more than 0.2 percent.

5. Analysis of the weight loss record

After completion of the run, the chart record, removed from the recorder, is divided so that the several traverses are separated from each other. The chart segments are then assembled to provide an effectively continuous trace representing the weight loss throughout the run, as shown in Figure 12.

The horizontal and vertical grids on one segment are carefully aligned parallel, respectively, to the horizontal and vertical grids on the next segment so that any deviations caused by tare weighting could be noted. None were ever noted; it is concluded that tare weighting did not noticeably affect the electronic measuring circuit or the apparatus as a whole. Once the chart segments are pieced together, the curve is taped to a flat surface and examined from either end by sighting along the curve at an acute angle to the surface. In this manner

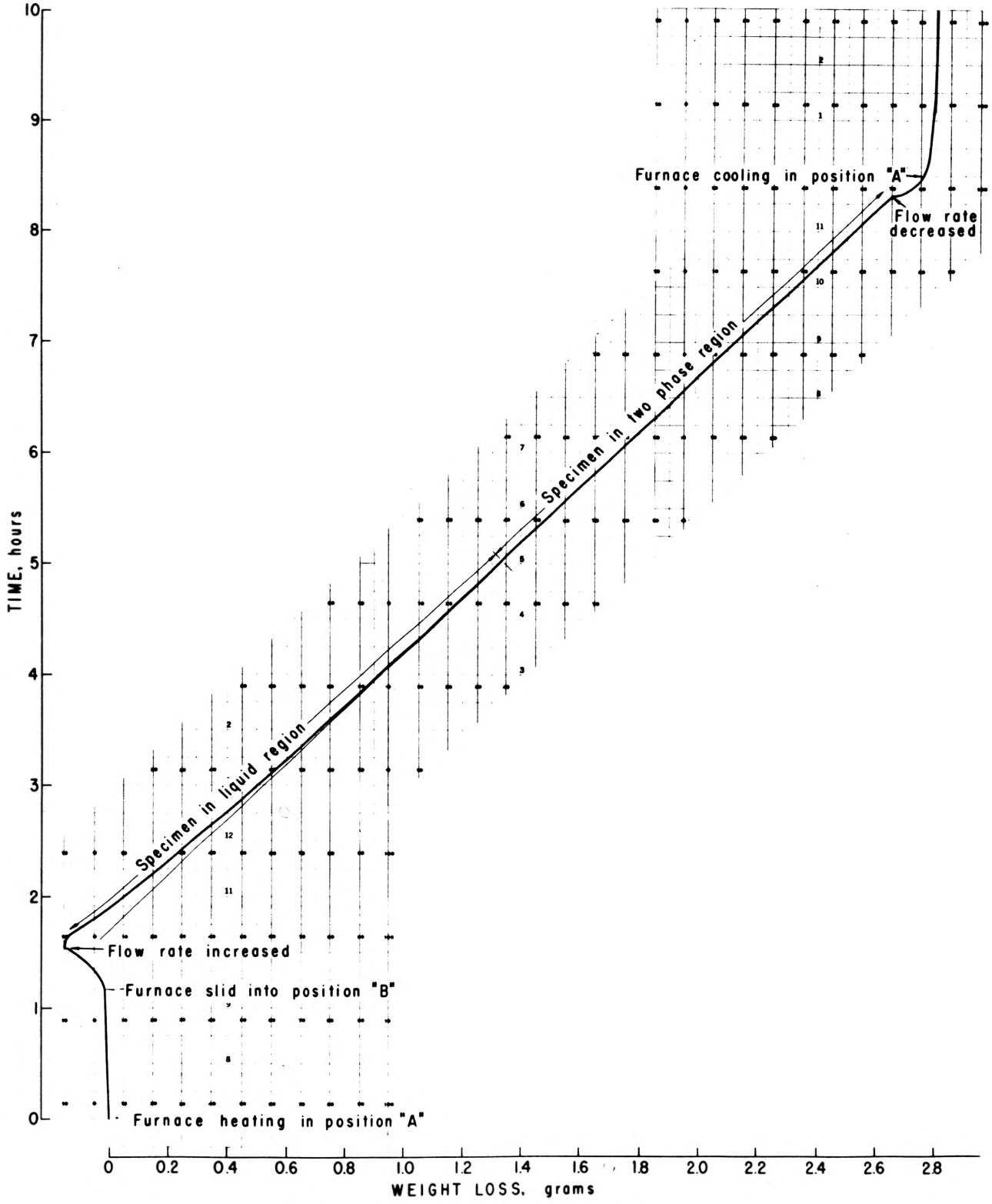

FIGURE 12.- Idealized Specimen Weight Loss Record.

the point of deviation from the straight portion could easily be detected. The location of the point of deviation was then re-determined with the aid of a long straight edge. Both methods indicated the same location for the point, usually within 5 small chart divisions.

The apparent weight gain during the sample heating period as noted in the initial portion of Figure 12 was caused by thermal expansion of the ceramic lever arm. The expansion increased the mechanical leverage from 2.740 at room temperature, to 2.762 at the temperature of the experiment (between 600° to 800° C). Thus the appearance of a weight gain was given on the chart record.

The apparent weight gain was recovered during the cooling period when the lever arm contracted to its original size.

The total weight loss of the sample is represented by the total distance between the room temperature records; that is, before and after the sample heating period.

Since there is no direct record of the weight loss during heating and cooling it is assumed that they are equal. The maximum error that could be introduced by this assumption is 0.01 to 0.5 grams per specimen, depending upon the vapor pressure of the alloy.

C. Results and Discussion

In order to evaluate the apparatus, five alloy systems were chosen that give a wide range of vapor pressures. Since the apparatus design is a modification of that used in the transport method of vapor pressure measurement, it was decided to study three alloy systems that have vapor pressures in the range in which the transport method is generally applicable. The accepted range is generally between 10^{-1} mm Hg and 10 mm Hg.

The remaining two alloy systems chosen exhibited vapor pressures greater than those in this accepted range to determine whether the apparatus was applicable to systems of higher vapor pressures.

1. Magnesium-nickel

The magnesium-nickel system was chosen because the vapor pressures of a number of magnesium-nickel alloys have been studied by means of the transport method.[14] In addition to this, the magnesium-nickel phase diagram[18] has been adequately established. Figure 13 shows the magnesium-nickel phase diagram as shown in the Metals Handbook.[19]* The temperatures of the experiments are designated on the diagram.

Four specimens were used in the series, each having the initial composition of 30.5 percent nickel, balance magnesium. The first of these was volatilized at 708° C and underwent a compositional change from 30.5 percent nickel to 43.7 percent nickel. This corresponds to a change in vapor pressure from 6.4 mm Hg to 5.7 mm Hg and a reduction in the rate of weight loss from 0.180 grams per hour initially to 0.143 grams per hour in the two-phase region. The initial rate is higher than is to be expected, since the temperature of the specimen generally increases to a maximum and then stabilizes at a temperature somewhat less than this maximum. In this case the maximum was 10° C higher than the stabilized chamber temperature of 708° C. This additional temperature rise gives pure magnesium an increase in vapor pressure from 10.3 mm Hg to 12.1 mm Hg, of approximately 16 percent. Therefore, until the system has reached a stabilized temperature, the actual rate of weight loss is

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*NOTE

The diagrams taken from the Metals Handbook are purely illustrative; the actual values were taken from the original papers.

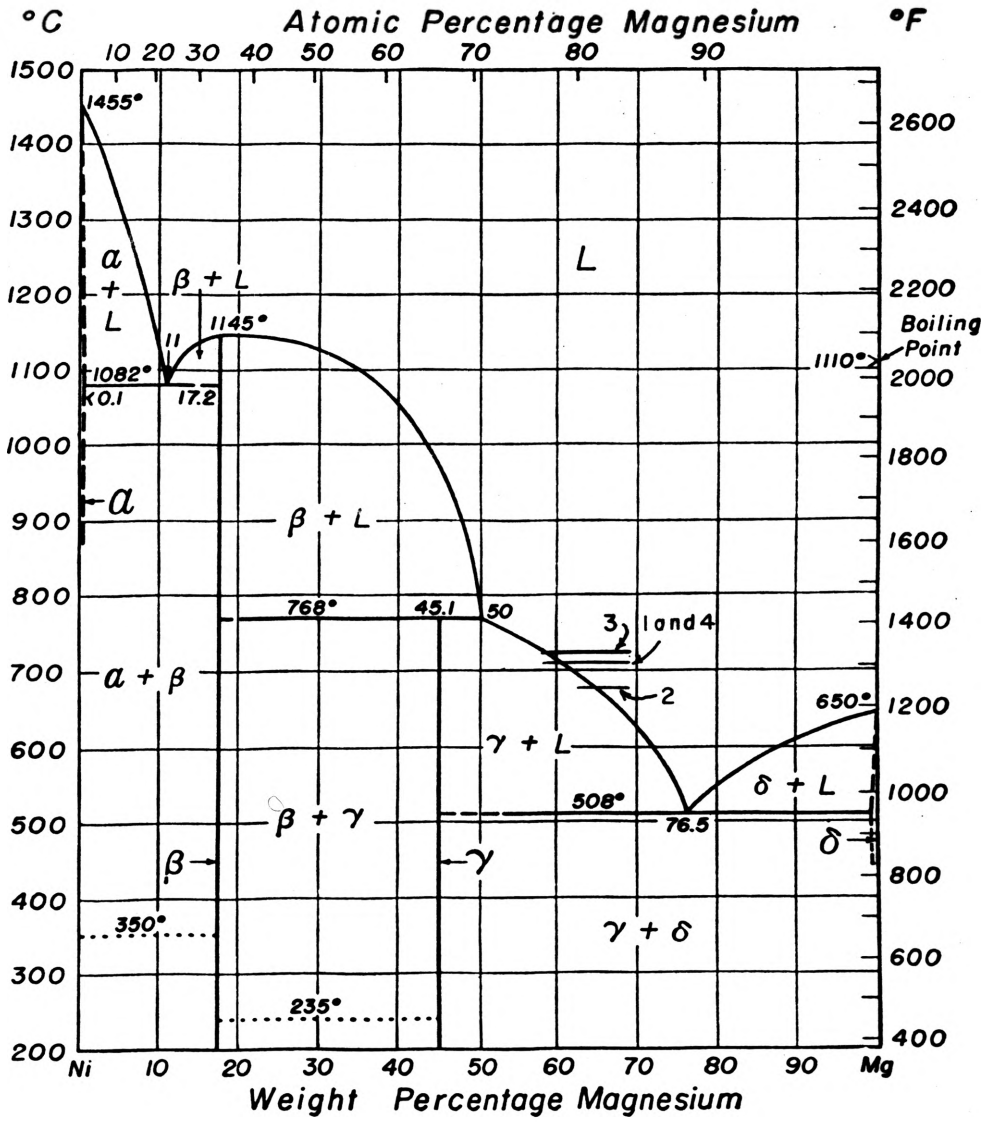

FIGURE 13.–Magnesium-Nickel Phase Diagram

meaningless. During the composition change, the specimen passed from the liquid region through the liquidus and into the liquid plus Mg_2Ni region before the experiment was terminated.

The total time of the experiment was 23 hours. The temperature during this time interval fluctuated between 707° C and 709° C. This temperature fluctuation is noted on the weight-loss record by the appearance of irregular changes in the rate of weight loss. In this case, a two-degree fluctuation in temperature is equivalent to a weight-percent change of approximately 2.7 in the nickel content of the liquidus, indicating the need for good temperature control.

Upon completion of the experiment, the weight-loss record was examined, and it revealed that the point of deviation is at 38.7 percent nickel, which is in agreement with the established phase diagram[18] showing 38.4 percent nickel.

The rates of weight loss were then measured at a number of compositions to test the possibility of using the apparatus for activity measurements. In order to avoid the effects of temperature fluctuation, the rate of weight loss was measured at one-hour intervals, as shown in Table III. They were then plotted versus time in hours from an arbitrary starting point (Figure 14). Here a smooth curve is drawn which best represents the group points, and values of the rate of weight loss are then taken from the curve.

In using the rate of weight loss to calculate the activities, it was assumed that the parameters of the system, together with the gaseous diffusion coefficient, remained constant. Thus, if these assumptions are correct, a ratio of the rate of weight losses at certain compositions should be equal to the ratio of the activities at those compo-

TABLE III

Rate of weight loss data for the magnesium-nickel experiments

Experiment 1		Experiment 2		Experiment 3		Experiment 4	
Hours	Rate of weight loss X 10^2	Hours	Rate of weight loss	Hours	Rate of weight loss	Hours	Rate of weight loss
1	17.1	1		1	14.3	1	13.0
2	10.0	2	9.5	2	14.5	2	12.4
3	17.5	3		3	14.7	3	12.2
4	16.8	4	8.1	4	14.7	4	12.0
5	16.8	5		5	14.2	5	11.9
6	16.2	6	7.8	6	13.9	6	11.7
7	16.2	7		7	13.8	7	11.2
8	16.5	8	7.8	8	14.5	8	11.0
9	16.1	9		9	14.3	9	10.6
10	15.8	10	7.6	10	13.8	10	10.5
11	15.4	11		11	13.6	11	10.3
12	15.0	12	7.3	12	13.3	12	10.2
13	15.0	13		13	13.4	13	10.1
14	15.5	14	7.7	14	13.3	14	10.0
15	15.5	15		15	13.4	15	9.9
16	15.0	16	7.6	16	13.5	16	9.7
17	14.7	17		17	13.4	17	9.6
18	14.5	18	7.5	18	13.2	18	9.6
19	14.3	19		19	13.0	19	9.6
20	14.3	20	7.4	20	12.9	20	9.6
21	14.4	21		21	12.7	21	9.6
22	14.3	22	7.2	22	12.6	22	9.6
23	14.3	23		23	12.6	23	9.6
		24	7.2	24	12.5		
		25		25	12.4		
		26	7.2	26	12.5		
		27		27	12.2		
		28	7.3	28			

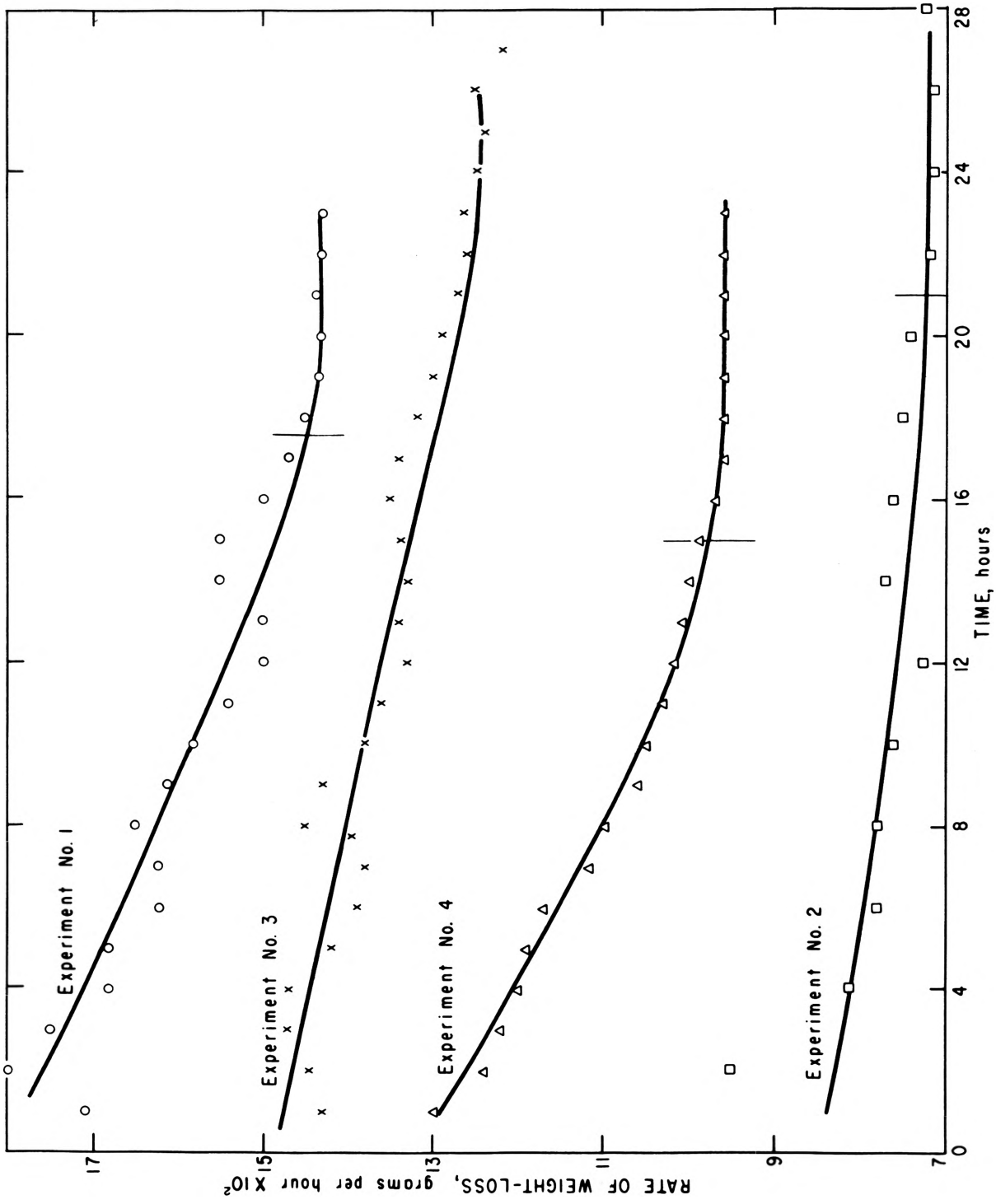

FIGURE 14.- Rate of Weight-Loss Versus Hours.

sitions. Therefore, if the activity of the system is known at one of the compositions, the remaining activities can be calculated with the ratios of the rate of weight loss.

The known activity, calculated from the work of Schmahl and Sieben,[14] is for magnesium in Mg_2Ni at the temperature of the experiment. This is also the activity of the magnesium in the two-phase region of the liquid plus Mg_2Ni. Thus, the rate of weight loss of the system during the straight portion corresponds to this known activity, and the activities of the system in the liquid region can be calculated from the ratios of rate of weight loss, as shown in Table IV.

Figure 15 is a plot of activity versus mole fraction of magnesium at various temperatures. The activity of the system, at the temperature and composition of the liquidus, is calculated from the work of Schmahl and Sieben,[14] and the remaining activities are calculated from the ratios of the rate of weight loss. The activities of the system at 750° C[14] are also included for comparison. It can be seen that the slope of the activity curve at 708° C is greater than the slope of the activity curve at 750° C. This is in agreement with systems containing intermetallic compounds. These systems generally show greater departures from ideality with decreasing temperature and decreasing mole fraction of the component for which the activity is being measured.

After the experiment, the specimen was sectioned and portions of it analyzed chemically. The analysis from Experiment No. 1 reported 42.0 percent nickel, whereas the calculated value from the weight loss was 42.3 percent nickel.

TABLE IV

Activity calculations from rate of weight loss ratios

Experiment	Composition	Weight percent nickel	Atomic percent nickel	Rate of weight loss grams per hour	Ratio	Ratio of rate of weight loss	Known activity	Calculated activities
1 (708° C)	1	33.4	17.2	0.166	1 to 3	1.085		0.528
	2	36.4	19.2	0.154	2 to 3	1.048		0.490
	3	38.7	20.8	0.143			0.456	
2 (676° C)	1	32.0	16.3	0.0800	1 to 2	1.119		0.462
	2	34.8	18.2	0.0715			0.412	
3 (721° C)	1	34.1	17.7	0.138	1 to 4	1.113		0.528
	2	36.0	18.9	0.133	2 to 4	1.064		0.504
	3	37.7	20.1	0.128	3 to 4	1.025		0.486
	4	39.4	21.2	0.127			0.474	
4 (706° C)	1	34.3	17.8	0.110	1 to 4	1.146		0.520
	2	35.8	18.8	0.104	2 to 4	1.088		0.492
	3	37.3	19.2	0.099	3 to 4	1.031		0.468
	4	38.1	20.3	0.096			0.454	

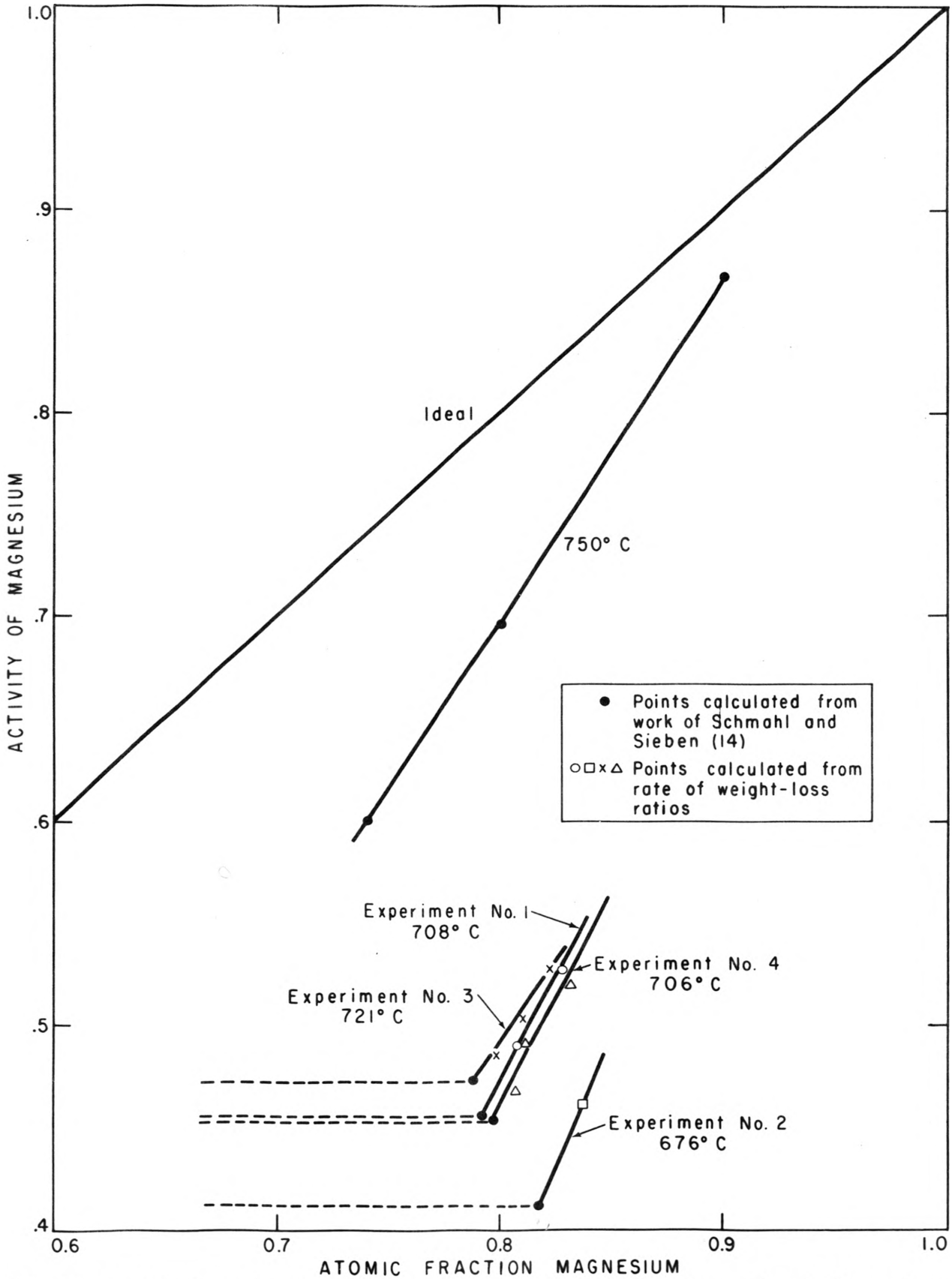

FIGURE 15 - Activity of Magnesium Versus Atomic Fraction Magnesium in Magnesium-Nickel System.

The remainder of the sample was metallographically examined for evidence of concentration gradients. None were noted, as can be seen in Figures 16 and 17. Figure 16 is a photomicrograph of the exposed surface; Figure 17 is a photomicrograph of the base of the specimen. The light portions are the intermetallic compound Mg_2Ni, and the dark matrix is the eutectic.

Experiment No. 2 was conducted at a lower temperature (676° C) and through a smaller composition change, from 30.5 percent nickel to 35.7 percent nickel. The corresponding approximate vapor pressure[14] and rate of changes of weight loss were from 3.8 mm Hg to 3.5 mm Hg and from 0.0784 grams per hour to 0.0706 grams per hour, respectively.

The small change in rate of weight loss, together with temperature fluctuations, made it difficult to distinguish the point of deviation. The first true departure from the straight portion of the curve was noted at 34.7 percent nickel, in agreement with the established phase diagram,[18] which shows 34.1 percent nickel.

The average rate of weight loss, taken from Figure 14, was then used to calculate the activity of the system at 676° C, as shown in Table IV. It will be noted in Figure 15 that the slope of the activity curve at 676° C is greater than that at 708° C or 750° C, in general agreement with systems containing intermetallic compounds.

During Experiment No. 3, conducted at 721° C, the specimen changed in composition from 30.5 percent nickel to 43.1 percent nickel. The corresponding vapor pressure and rate of changes of weight loss were from 7.7 mm Hg to 6.5 mm Hg and from 0.138 grams per hour to 0.115 grams per hour, respectively.

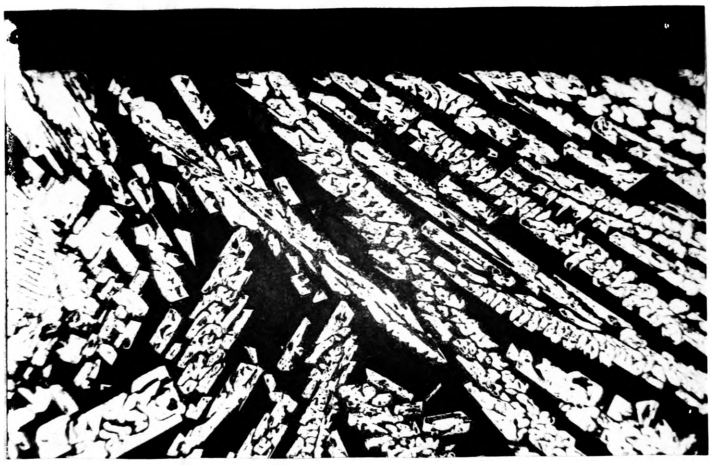

FIGURE 16. Exposed Surface of Mg - 43.7 Percent Ni After Volatilization, Mechanically Polished, Unetched. X 25

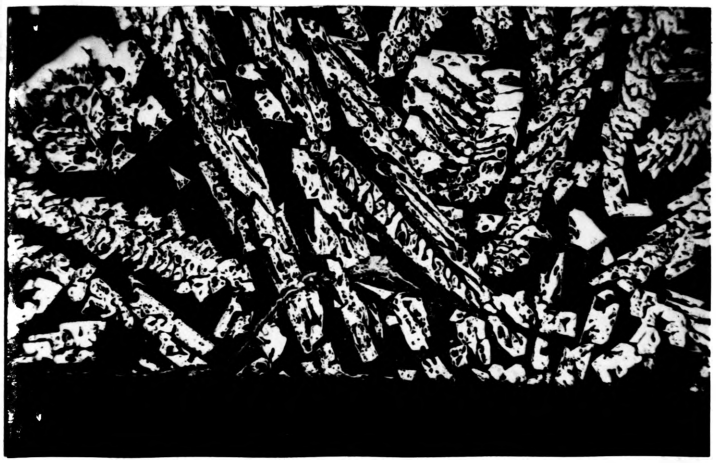

FIGURE 17. Base of Mg - 43.7 Percent Ni After Volatilization, Mechanically Polished, Unetched. X 25

Examination of the weight-loss record revealed a straight portion that was too short in length to be conclusive; therefore, the record was not used in the establishment of the liquidus. However, the ratios of the rate of weight losses were used to calculate the activities of the system at 721° C; the results are tabulated in Table IV.

It will be noted in Figure 15 that the slope is greater than that of the activity curve at 750° C but not as great as that of those at the lower temperatures; this is in agreement with the results of preceding experiments.

In Experiment No. 4, conducted at a temperature of 706° C, the temperature fluctuations were kept to a minimum. This is brought out clearly by Figure 14, which shows that the actual measured rates of weight loss vary only slightly from the curve of the average value.

The composition of the specimen changed from 30.5 percent nickel to 43.1 percent nickel, with the corresponding vapor pressure and rate of weight loss changing from 6.2 mm Hg to 5.5 mm Hg and 0.130 grams per hour to 0.096 grams per hour, respectively.

Upon completion of the experiment, the weight-loss record was examined, and it revealed that the point of deviation is at 38.1 percent nickel, in agreement with the established phase diagram,[18] which also shows 38.1 percent nickel.

The average rate of weight loss, shown in Figure 14, was then used to calculate the activity of the system at 706° C in Table IV. Again, the general slope of the activity curve, shown in Figure 15, is in agreement with those of the previous experiments.

2. Copper-zinc

A copper-zinc series was chosen because of the high vapor pressures encountered within the system, and also because the copper-zinc phase diagram[20] is well established. Figure 18 is the copper-zinc phase diagram from the Metals Handbook.[21] The average temperature of the experiments is denoted on the diagram. The two specimens used in the series had the composition of 75.4 percent zinc, balance copper.

During the first experiment, conducted at a temperature of 788° C, the specimen underwent a compositional change from 24.6 percent copper to 33 percent copper and passed from the liquid region into the liquid plus gamma region. Because of the high vapor pressures of the alloys (from 195 mm to 145 mm Hg),[22] large rates of weight loss were encountered. For example, at the beginning of volatilization the rate was 4.049 grams per hour, and it gradually decreased to 2.400 grams per hour in the liquid plus gamma region.

Upon completion of the experiment the weight-loss record was examined; it revealed a short, straight portion beginning at 30.5 percent copper, in agreement with the accepted copper-zinc phase diagram,[20] which shows the location of the liquidus at approximately 31 percent copper. An irregular section was also noted immediately following the straight portion. It started at 31.4 percent copper and continued with the same average slope as that of the straight portion, until the termination of the experiment. Alternate depletion and replenishment of zinc at the surface is probably the source of the irregularity.

The fluctuating surface concentration could be brought about by the formation of a surface layer of the precipitating solid phase, which upon

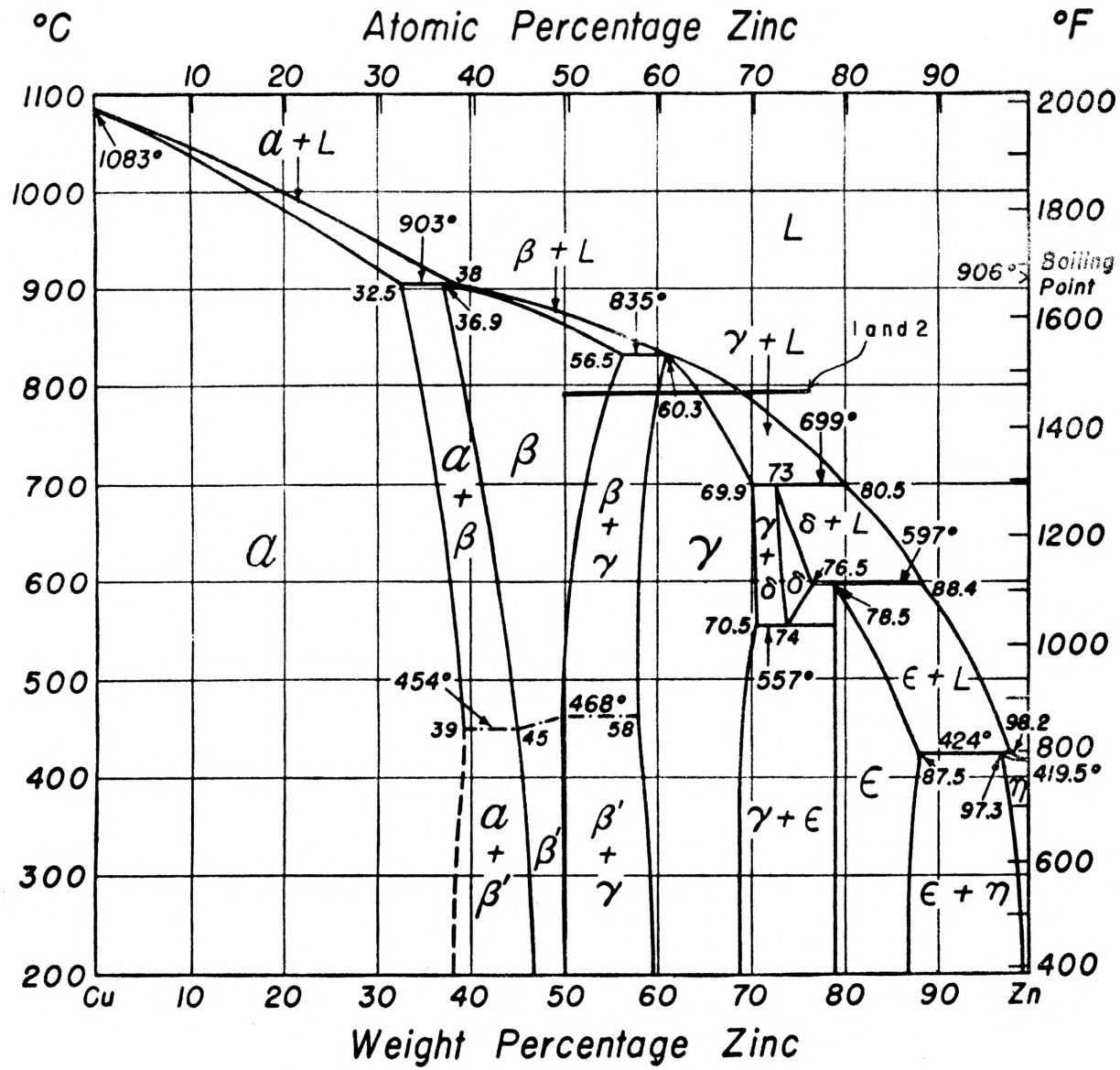

FIGURE 18.-Copper-Zinc Phase Diagram.

further volatilization contracts and fractures, exposing a fresh liquid surface. If contraction continues, the liquid would be forced out of the fracture, redistributing the mass in the crucible and thereby changing the center of gravity of the specimen. This in turn would change the lever arm of the sample, causing an apparent weight gain or loss in the same manner as the expansion or contraction of the ceramic lever arm does during heating or cooling. Figure 19 shows an example of surface layer formation in a copper-cadmium specimen. The dark portion is the copper-rich alpha solid solution which is the precipitated phase, and the light matrix represents the liquid portion. It will be noted at point 1 that the presence of a surface layer of a copper-rich phase has caused the underlying liquid to erupt at point 2, forming the irregular surface.

The second copper-zinc experiment was performed at a slightly higher temperature (790° C) and over a larger composition range (24.6 percent copper to 49.6 percent copper). This experiment caused the system to progress through the gamma region, the gamma plus beta region, and into the beta region, in addition to the liquid and liquid plus gamma regions investigated in the first experiment. Also a wider range of vapor pressures was encountered during this experiment, from 195 mm to 65 mm Hg,[22] as well as a wider range of rates of weight losses, from 2.90 grams per hour to 1.09 grams per hour.

In order to increase the time between tare weighting, the recorder span was compressed from 1 gram full scale to 2 grams full scale and the argon flow reduced slightly. As a consequence, the sensitivity of the apparatus was reduced by a factor of 2.

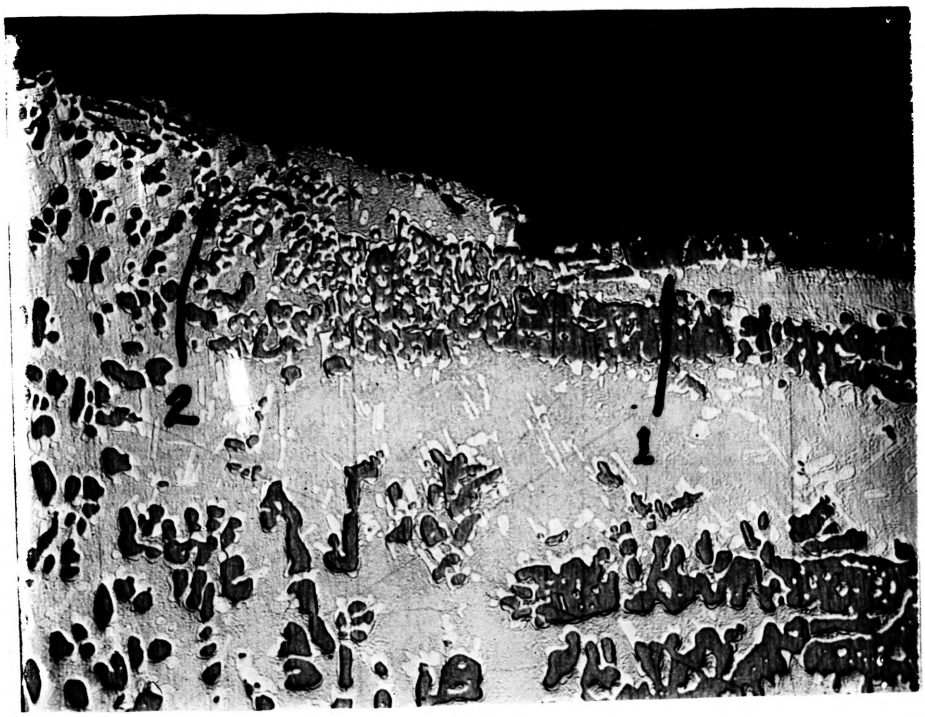

FIGURE 19. Exposed Surface of Copper - 46.9 Percent Cadmium After Volatilization, Mechanically Polished, Unetched. X 75

Examination of the completed weight loss record revealed the absence of any well-defined straight portions, although, as in the previous experiment, irregular portions appeared within both of the calculated two-phase regions. As before, the irregular portions had the same average slope throughout their respective two-phase regions; this slope was proportional to the characteristic vapor pressure of the region. The irregular portions in the liquid plus gamma region and the solid gamma plus beta region extended from 31.2 to 33 percent copper and from 42.6 to 46 percent copper, respectively. The accepted boundaries are 31 to 34 percent copper[20] and 41 to 45 percent copper,[20] respectively. Compression of the recorder span was probably the reason for the absence of any noticeably straight portions in the weight-loss record.

3. Copper-cadmium

The copper-cadmium system was chosen because moderately high vapor pressures are exhibited by a number of the alloys, and the binary diagram[23] is reasonably well established. Figure 20 is the copper-cadmium phase diagram as represented in the Metals Handbook.[24] The temperatures of the experiment are marked on the diagram.

A 40.4 percent copper alloy was chosen because its vapor-pressure range extends lower than that of the copper-zinc series, and it also exhibits a large compositional change between the liquidus and solidus, thereby reducing the proportion of solid formed per unit of weight lost.

Two specimens were included in the series. The first was volatilized at 648° C with an initial vapor pressure of approximately 90 mm Hg.[25] The initial rate of weight loss was approximately 2.96 grams per hour, decreasing to 2.28 grams per hour in the final portions of the record.

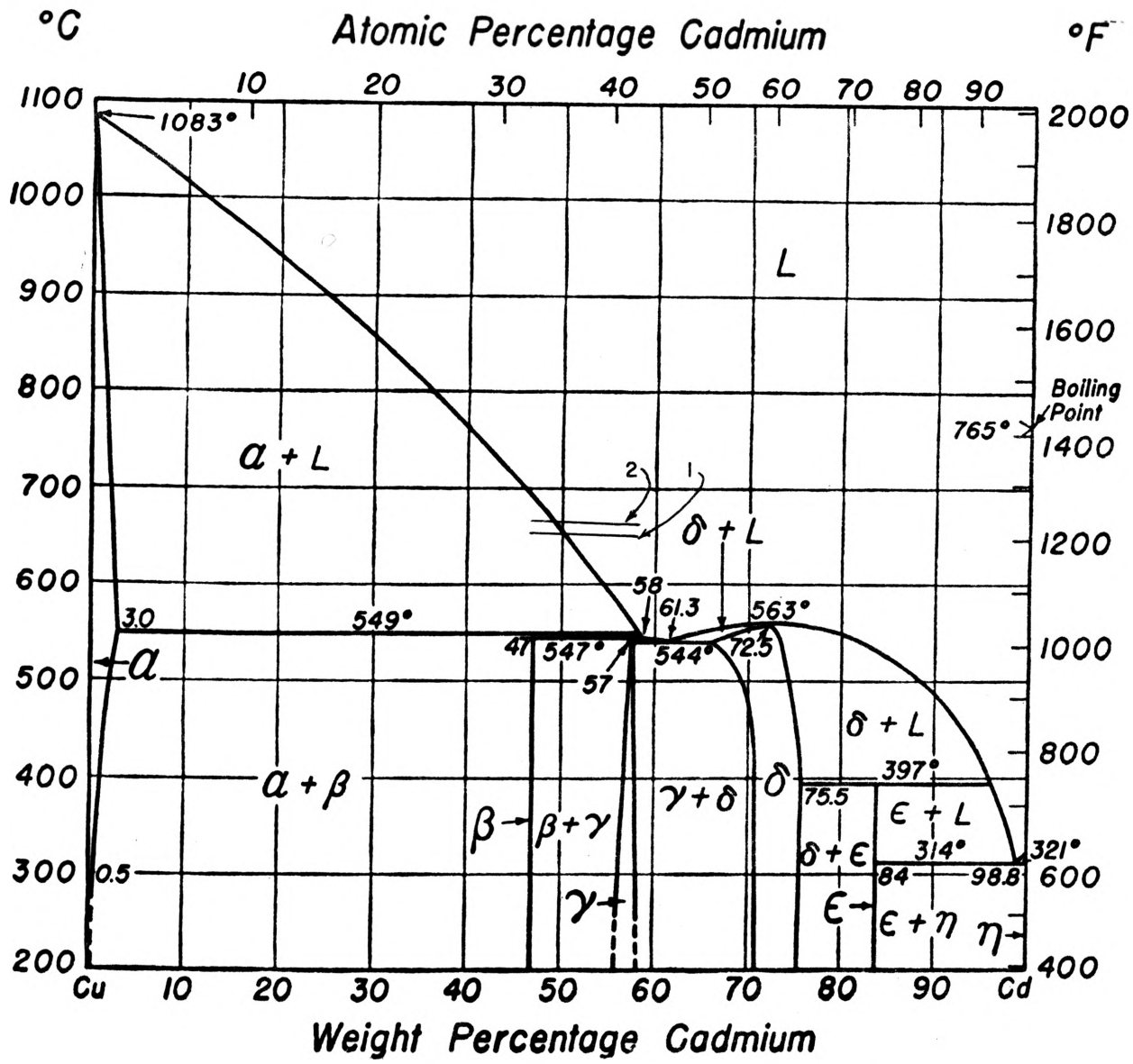

FIGURE 20.- Copper-Cadmium Phase Diagram.

This rate is slightly greater than was that of the second copper-zinc experiment, even though the vapor pressure of cadmium was approximately one half that of zinc. This was promoted by the large atomic mass of cadmium (112.41), almost twice that of zinc (65.38).

Examination of the weight-loss record revealed an irregular fluctuation throughout that was similar to that noted in the two-phase portions of the copper-zinc system, but the curve did not exhibit the same general slope throughout. This indicated surface depletion of the cadmium and the formation of the copper-rich alpha phase during the time the specimen is brought up to temperature. This surface layer probably never is dissolved by the liquid, even though the specimen should be well within the liquid region. It would appear as though the rate of volatilization from the surface was too great to allow dissolution of the surface layer, and that the surface layer itself was probably a solid solution containing very small quantities of cadmium. Under these circumstances the surface layer possesses a much higher melting point than the solid solution supposedly in equilibrium with the liquid at 648° C. Figure 19, a photomicrograph of a copper-cadmium alloy after volatilization, seems to verify this explanation. Here, the surface layer probably broke to expose the underlying liquid rather than dissolve in the liquid. This would also explain the generally decreasing slope. The underlying liquid, not having reached the composition of the liquidus, would be continuously changing in the composition. Thus the changing composition reduces the vapor pressure and in turn the rate of weight loss.

In an attempt to dissolve this surface layer, the second experiment was performed at a slightly higher temperature (662° C) at which dissolution should be aided by more rapid diffusion, as well as by the

increased free energy drive caused by greater departures from equilibrium. Examination of the record revealed no change in its appearance; this indicates that the kinetics of the dissolution is much slower than the kinetics of volatilization, so that the coating over the liquid is persistent.

4. Cadmium-antimony

An alloy containing 31.3 percent cadmium, balance antimony, was made to evaluate the operation of the equipment at low vapor pressures. Activity calculations[26] indicated an estimated vapor pressure of 1.2 mm Hg for this alloy. Caution was necessary in using this estimation, since the thermochemical data were said to contain a number of discrepancies.

One specimen, which lost 0.0002 grams per hour, was tested. This rate seems much lower than one would expect for an alloy with this vapor pressure; therefore, it would appear as though the thermochemical data are in error in this particular case.

5. Magnesium-zirconium

A number of investigations[27] of the magnesium-zirconium system have been carried on by conventional methods, with no general agreement as to the location of the liquidus. Part of this disagreement arises from the weight losses encountered during the experiments.

The weight-loss technique for determining phase boundaries would eliminate this complication, as it utilizes weight loss for the determination. With this in mind, a magnesium-zirconium series was set up to disclose whether the liquidus could be located by using the weight-loss recording apparatus.

Sixteen specimens were used in a series which ranged in composition from 0.2 to 0.47 percent zirconium. The experiments were conducted at temperatures between 750° and 800° C, with the rate of weight loss ranging from approximately 0.33 to 0.62 grams per hour. The large differences in the rate exist because of the large changes in vapor pressure with temperatures, from 15.8 mm Hg at 750° C to 31.4 mm Hg at 800° C.[14] The experiments can be grouped into two categories according to the type of crucible wash used during the experiment, those with an oxide wash and those with a carbon wash. The effects of the wash on the surface tension and zirconium content of the specimen were the cause of the differences in results noted for the two categories.

The surface tension of the specimen with respect to the oxide wash was large enough to cause it to withdraw from the crucible sides and assume an irregular ellipsoidal shape. In so doing, the area as well as the center of gravity of the specimen would be constantly changing and thereby adversely affecting the weight-loss record. Carbon washes, on the other hand, allowed the specimen to climb the side of the crucible, producing a concave surface which would remain relatively constant in area and location throughout the remainder of the experiment.

Although the carbon solves the constant area problem, chemical and metallographic analyses indicated that the carbon depleted the specimen of zirconium, perhaps by a carbide formation reaction along the sides of the crucible. Figures 21, 22, and 23 are photomicrographs of magnesium-zirconium specimens, and they serve to illustrate the zirconium depletion. Figure 21, a photomicrograph of 0.47 percent zirconium specimen before volatilization, shows the typical fine-grain structure observed in

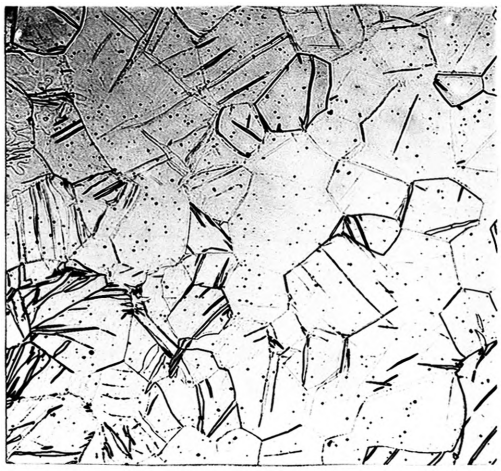

FIGURE 21

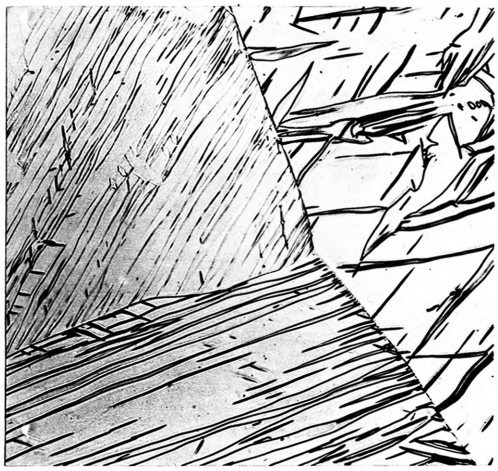

FIGURE 22

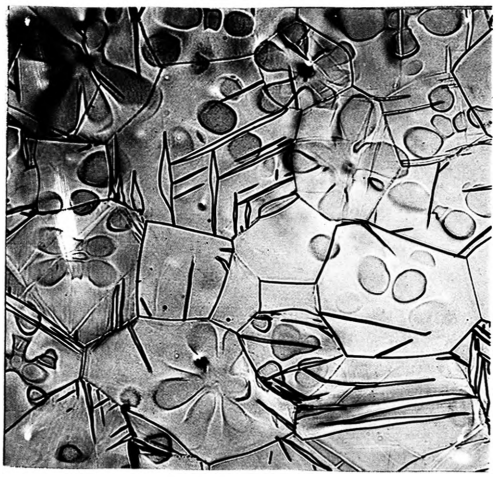

FIGURE 23

FIGURE 21. Mg - 0.47 Percent Zr Chemical Analysis, Before Volatilization, Electrolytically Polished, and Etched in Mg 12 for 10 Sec. X100

FIGURE 22. Mg - 0.65 Percent Zr Calculated Analysis - 0.36 Percent Zr Chemical Analysis, After Volatilization, Using Carbon Crucible Wash, Electrolytically Polished, and Etched in Mg 12 for 10 Sec. X100

FIGURE 23. Mg - 0.66 Percent Zr Calculated Analysis - 0.65 Percent Zr Chemical Analysis, After Volatilization, Using MgO Crucible Wash, Electrolytically Polished, and Etched in Mg 12 for 10 Sec. X100

magnesium-zirconium alloys of this composition. Figure 22, on the other hand, is a photomicrograph of a specimen after volatilization in a crucible washed with lampblack. The nominal zirconium content was 0.65 percent, but the specimen exhibits extremely large grains typical of those found in alloys containing approximately 0.3 percent zirconium. Chemical analysis of this specimen reported 0.36 percent zirconium, verifying metallographic analysis. Figure 23 is a photomicrograph of a specimen volatilized using a magnesium oxide wash. Here, a number of the cored areas show at their centers the nucleating particles of zirconium-rich phase. The nominal zirconium content here was 0.66 percent, which is in agreement with the chemical analysis of 0.65 percent zirconium.

Examination of the weight-loss records of those specimens volatilized in the oxide wash revealed that the effects of the changing area and center of gravity were greater than the effects of changing composition (usually in the vicinity of 0.2 atomic percent). Thus, the record generally consisted of a relatively straight line with small irregular deviations superimposed upon it.

Weight-loss records of the carbon wash series, on the other hand, showed the anticipated decreasing rate of weight loss, and in two cases, exhibited a long straight portion. In one of the experiments performed at 800° C and a flow rate of 500 cc per minute, the record indicated supersaturation similar to the type encountered by Velickis, Rosen, and Feder.[15] That is, a gradually decreasing rate of weight loss is followed by an abrupt increase in the rate, which then remains constant throughout the remainder of the record. This abrupt change probably represents the precipitating phase or phases that reduced the degrees of freedom of the system to 1, the necessary condition for a straight line.

IV. SUMMARY AND CONCLUSIONS

A. Limitations and Capabilities of the Apparatus

The results of all experiments in the alloy systems investigated in this research indicate that the apparatus designed in this work to determine phase boundaries in binary alloy systems has certain limitations and, at the same time, certain capabilities.

1. Limitations

a. Vapor pressure range

From the results of the magnesium-nickel experiments and the magnesium-zirconium experiment at 800° C, it appears that the apparatus is capable of detecting phase boundaries in binary systems with vapor pressures of one volatile component in the range of 3 to 35 mm Hg. Below this range, the time required to give composition changes of any magnitude is exceedingly long. Above this range, surface depletion is likely to occur, as was brought out clearly by the results of the copper-cadmium system.

b. Argon flow rates

Argon flow rates within the range of 200 to 500 cc per minute do not appear to have a significant effect on the determination of phase boundaries. This is exemplified by the copper-zinc and copper-cadmium systems, which showed surface depletion at a flow rate of 200 cc per minute, and by the magnesium-nickel and magnesium-zirconium systems, which exhibit both the curved and straight portions, even though the flow rates ranged from 425 to 500 cc per minute. Experience has shown that beyond 500 cc per minute, the flow of argon adversely affects the surface of the specimen, whereas below 200 cc per minute there is a possibility for back diffusion of the metal vapor.

c. Limits of sample weight change

Experience has shown that a specimen loss of less than 25 percent of the total volume is optimum. Beyond this optimum, surface tension might cause the specimen to change in shape and exposed area. However, in certain cases as much as 50 percent of the total volume of the specimen can be lost, with no adverse effects on the results.

d. Factors affecting rate of weight loss

The magnesium-zirconium experiments indicate that in certain systems the changing compositional effects on the rate of weight loss are overshadowed by side effects such as area, center of gravity, and temperature changes.

e. Summary of results

Table V gives a summary of data for the various experiments performed.

2. Capabilities

a. Oxidation of specimens

Work with the highly reactive systems of magnesium-zirconium and magnesium-nickel has proved that the apparatus is capable of working with highly reactive systems at elevated temperatures without significant oxidation of the specimen.

b. Activity measurement

The magnesium-nickel series showed the possibility of using the apparatus for activity determination. This method would be extremely convenient, as it would eliminate a large number of experiments that are now needed to determine the activity of a system over a range of composition.

TABLE V

Summary of experimental data

System	No.	Temperature ° C	Approx. vapor pressure mm Hg	Weight loss gms/hr	Comp. change percent	Flow rate cc/min	Recorder span gm/100 div.	Remarks
Cu-Zn	1	788	195 - 145	4.049 - 2.400	24.6 33	250	1	Small straight portion noted 30.5 surface depletion
	2	790	195 - 145	2.90 - 2.10	24.6 31.2	200	2	No true straight portion surface depletion
			145 - 85	2.10 - 1.29	33 42.6			
			85 - 65	1.29 - 1.09	42.6 49.6			
Cu-Cd	1	662	100 - 90	4.44 - 3.60	40.4 45.3	200	1	No straight portion surface depletion
	2	648	100 - 70	2.96 - 2.28	40.4 53.1	200	1	No straight portion surface depletion
Mg-Zr	Ox	750 - 770	11 - 18	0.265 - 0.333	0.3 0.8	365 - 500	1	Surface effects predominate
	C	750 - 800	11 - 31	0.268 - 0.650	0.3 0.8	365 - 500	1	Zirconium depletion super saturation noted
Mg-Ni	1	708	7.8 - 6.7	0.80 - 0.143	30.5 42.3	437	1	Curve and straight portion, deviation starts at 38.7 percent Ni
	2	676	4.7 - 6.5	0.0784 - 0.0706	30.5 35.8	425	1	Curve and straight portion not well defined, deviation 34.7 percent Ni
	3	722	7.7 - 6.5	0.138 - 0.115	30.5 43.1	425	1	No deviation noted
	4	706	6.2 - 5.5	0.130 - 0.096	30.5 43.1	425	1	Curve and straight portion, deviation 38.1 percent Ni
Cd-Sb	1	538	1.2	0.0002	--	300	1	Apparently vapor pressure lower than 1.2 mm Hg

c. Stability of the apparatus

The magnesium-nickel series showed that the system was relatively stable during the 23-hour experiments, as well as over large composition changes.

B. Conclusions

On the basis of this research, it is concluded that a technique for determining phase boundaries by measuring the rate of weight loss is feasible; a technique has been validated for the magnesium-nickel alloy system.

The apparatus is best suited for systems exhibiting vapor pressures between the limits of 3 and 35 mm Hg. Below this limit, the time needed to change the concentration significantly becomes impractical; above this limit, the kinetics of vaporization and diffusion tend to give erroneous results. The maximum working temperature for the apparatus is approximately 1000° C. The stability of the system is good over long periods of time as well as large compositional changes. The possibility of using the equipment for activity determinations has been shown. The utility of the apparatus for highly reactive materials at elevated temperatures has been demonstrated by the absence of oxidation.

It has also been shown that, under the proper conditions, approximate phase boundaries can be located in systems with vapor pressures higher than those within the suitable range of the equipment, but only with proper precautions in analyzing these results.

V. SUGGESTED FURTHER RESEARCH

The parameters of the apparatus should be studied in order to use it for quantitative activity calculations. In this way, the apparatus could be used to determine phase boundaries, and at the same time to determine the activities of the components of the system.

Because of the design, the apparatus becomes a useful tool in determining the validity of a number of the assumptions used in the transport technique to calculate vapor pressures. One of these assumptions is that the saturation of the carrier gas with metal vapor is independent of the carrier gas flow rate beyond a certain minimum.

The apparatus itself is not limited to activity studies or phase-boundary determination but would be very useful in elevated-temperature studies of kinetic reactions between liquids or solids and a controlled gas atmosphere.

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VII. VITA

Robert Lee Benner was born on December 9, 1933, in Elizabeth, New Jersey. Mr. Benner attended grade school in Denville, New Jersey, and upon graduation from Dover High School, he served a two-year apprenticeship as a tool and die maker. From June 1953 until June 1957 he served in the United States Navy as a Machinery Repairman. In September 1957 he was enrolled at Missouri School of Mines and Metallurgy and received his B.S. degree in Metallurgical Engineering in May 1961. Mr. Benner then began the research presented here at the United States Bureau of Mines under the auspices of a Bureau of Mines Cooperative Fellowship.